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MARTIN MARIETTA

**CHEMISTRY DIVISION
ANNUAL PROGRESS REPORT
for Period Ending January 31, 1986**

OPERATED BY
MARTIN MARIETTA ENERGY SYSTEMS, INC.
FOR THE UNITED STATES
DEPARTMENT OF ENERGY

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for Period Ending January 31, 1986

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1. INTRODUCTION AND DIVISIONAL OVERVIEW

The Chemistry Division emphasizes research aimed at broadening the base of fundamental understanding of materials and phenomena of relevance to future energy technologies. It also conducts shorter-range studies of more immediate energy interest in cases where the expertise of its staff is appropriate. A broad range of chemical specialties is covered, except for analytical chemistry which is organizationally separate at ORNL. This Report briefly describes progress during the last year. Some selected highlights are listed here; the number in parentheses after each entry refers to the Section of the Report where more details can be found.

1. Development of a new internal standard technique for quantitation of CP/MAS ^{13}C NMR spectra of coal showed that only 40-60% of the carbons are detected in coals of widely varying rank. Furthermore, methylation of coal with $^{13,14}\text{C}$ double-labeled CH_3I , following deprotonation by bases of controlled strength, revealed that native coal carbon, introduced O-methyl carbon, and introduced C-methyl carbon are each detected with different sensitivity factors. (2.1.1)

2. New insights into effects of restricted diffusion of reactive intermediates during thermal reactions of coal were gained from studies of surface-attached model compounds. Surface immobilization substantially promoted free-radical chain pathways (rearrangement, cyclization, and hydrogenolysis) during thermolysis of bibenzyl which had been covalently bonded to an inert silica surface. (2.6)

3. Enthalpies of dilution of a strong base, aqueous NaOH, at high temperatures (to 400°C) were measured for the first time. Although ion association has been proposed in the literature to rationalize trends in activity coefficients for NaOH at much lower temperatures, the new results do not support this interpretation below 250°C. (3.1.2)

4. Osmotic coefficients for aqueous solutions of the alkali metal sulfates (M_2SO_4) were obtained to 225°C by isopiestic measurements, and the results were combined with other existing thermodynamic data to produce a comprehensive model. The much smaller activity coefficients, compared with those of the alkaline earth chlorides ($\text{M}'\text{Cl}_2$) which would have the same long-range electrostatic contributions, can be interpreted in terms of differences in hydration. (3.1.4)

5. Our previous experimental observations that changes in the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratios of rhyolite liquids are sluggish suggested that glassy rhyolites should preserve the pre-eruption redox signature of the parent magmas. This hypothesis has now been strengthened by examination of core samples of obsidian flows at Inyo Domes, California and Valles Caldera, New Mexico, both sites of DOE-sponsored Continental Scientific Drilling Projects. (4.1)

6. The ability to determine equilibrium constants for complexation between metal cations and various anions in aqueous solutions at temperatures to 300°C was demonstrated for ferrous ion, both by solubility measurements and by potentiometric titrations. The observation that ferrous--acetate complexes are about 1000 times stronger than competing chloride complexes lends further credence to our earlier hypothesis of a role of acetate and other organic complexing agents in metal migration in the Earth's crust. (4.2.4 and 4.2.5)

7. An effective electrocatalyst for Cl_2 evolution from acidic chloride solutions was prepared by ion implantation of Ru into a Ti substrate and subsequent anodic oxidation of this "near surface" Ru-Ti alloy to form a $\text{RuO}_2\text{-TiO}_2$ mixed oxide supported on Ti. In situ photoacoustic and photocurrent spectroscopies demonstrated that this mixed oxide exhibits the metallic-like conductivity essential for electrocatalysis. The mechanism of Cl_2 evolution was determined. (5.1.1-5.1.3)

8. Ammonolysis of titanium halides in liquid ammonia followed by reaction with sodium acetylide gave a series of Ti_4 cluster compounds having both N-containing and acetylide ligands. These precursors were converted at 800°C into titanium carbonitride ceramic powders whose C:N ratio reflected the composition of the precursor. (5.1.10)

9. Self-diffusion coefficients determined for polystyrene melts by small-angle neutron scattering were in qualitative agreement with a theoretical model for their functional dependence on the molecular weight of the polymer. However, their magnitudes differed significantly from those obtained earlier by others with an NMR technique; this suggests that these two experimental methods are sensitive to different types of motion. (5.2.2)

10. An approach was developed, based on a set of exact statistical mechanical equations, which promises to increase the accuracy and range of application of lattice fluid techniques for calculating the thermodynamic properties of polymer systems. (5.2.4)

11. Studies, in collaboration with LLNL, of spontaneous fission of the heaviest radionuclides (atomic numbers ≥ 100 and masses near 260) have revealed two simultaneous pathways for fission, one leading to symmetric and/or asymmetric fission with "normal" energies of about 200 MeV and a second leading to symmetric fission with notably higher energies of about 240 MeV. The realization of this new, general, as yet unexplained phenomenon was aided by our discovery of a new nuclide, ^{260}Md , with the rather long half-life of 32 days. (6.1.5)

12. Studies of the transformation of atomic, localized 5f electrons in the transplutonium metals into delocalized, bonding electrons by the application of very high pressures (to 50 GPa) were extended to Bk-Cf alloys. The characteristic crystal structures of the alloys at high pressures correspond to those of the major constituent of the alloy, and the required delocalization pressures are intermediate between those for the pure metals. (6.2.1)

13. An interactive general least-squares computer program was developed to facilitate identification of the numerous reaction products that form in the organic phase of synergistic solvent extraction systems as acidic and neutral extractants interact both with one another and with ions extracted from the aqueous phase. As an example of its application, vapor pressure osmometry and FTIR, NMR, and Raman spectroscopy data for the system Sr^{2+} --didodecylphthalenesulfonic acid (HX)--dicyclohexano-18-crown-6 ether (6)-- CCl_4 could be interpreted to indicate the formation of $SrX_2 \cdot B \cdot 2H_2O$ and $SrX_2 \cdot B \cdot HX \cdot nH_2O$ complexes with Sr bonded within the crown ether cavity. (7.2)

14. The X-ray crystal structures of the isolated solvent extraction complexes $(M^{2+})((RO)_2PO_2^-)_2^-$ (18-crown-6)(H_2O), where R = n-butyl and $M^{2+} = Ba^{2+}$ or Sr^{2+} , differ qualitatively only in the conformation of the crown ether. Molecular mechanics calculations showed that the geometry adopted by such flexible crowns as they complex cations of various sizes is determined primarily by electrostatic forces rather than by strain energy. (7.3)

15. Liquid chloroaluminate systems with high $AlCl_3$ activities have been prepared that are, for the first time, virtually free of protic and oxidizing impurities. Radical cations and dications of aromatic compounds proved to be exceptionally long-lived in these Lewis superacids. (8.1.1)

16. A new capability of low-energy ion scattering for surface structure determination was demonstrated by using the dependence of scattered Li^+ ion intensity from the clean Mo(111) surface on the incident angle to measure near-surface interplanar spacings. The first interlayer spacing was found to be contracted by 18% compared with the bulk for this bcc metal. (8.2.2)

17. New data on photoionization cross-sections and photoelectron angular distributions, obtained with synchrotron radiation, for the series of resonances found between the spin-orbit states of HI provide new insights into the fundamental concept of autoionization in molecules. Data which systematically define the Cooper minimum in the chloromethanes would appear to offer a valuable means for appraising the atomic makeup of molecular orbitals. Analogous phototelectron dynamics studies of metal atoms were extended from earlier data for s, p, and d electrons to f electrons as represented in ytterbium vapor. The satisfactory agreement observed with the most advanced theory available for this closed-shell atom gives added confidence in the predictive capabilities of the theory. (9.1 and 9.2.1)

18. Both experimental and assessment studies relating to safety analyses of proposed nuclear waste repositories were conducted. As one example, the solubilities of electrodeposited and precipitated Tc(IV) oxides were determined in several aqueous solutions and synthetic groundwaters in the pH range 1-10. These data will be useful for calculation of transport rates of technetium in nuclear repository environments. (10.1 and 10.3)

19. A systems analysis of ink chemistry and technology, as practiced at the Bureau of Engraving and Printing, was carried out with the aim of developing an AI-based heuristic reasoning system as the basis of a computer workstation for ink formulation. Considerable progress was made on an analytical solution to those factors related to color which will incorporate on-line reflectance measurements. (11.1.1)

20. To improve interpretation of small-angle neutron scattering data from water-in-oil microemulsion fuels and to avoid the approximation of equivalent spheres, an analytical expression was developed for the static structure function of a polydisperse fluid.

Summaries of staffing, organization, and funding sources are provided at the end of the Report. The major source of funding is the Office of Basic Energy Sciences of the Department of Energy (DOE), but work is also carried out for other parts of DOE, for the Nuclear Regulatory Commission, and for other Federal agencies. In addition to personnel shown on the Organization Chart, the productivity of the Division is enhanced by a significant number of University professor and student guests in a variety of guest assignments; these significant interactions are acknowledged individually in the text of the Report.

Additional information on any of the research programs described herein can be obtained by contacting individual staff members of the Division.

2. COAL CHEMISTRY

The goal of this fundamental research program on the organic chemistry of coal is an improved knowledge of the structure and reactivity of this complex material. A new internal standard procedure to measure the fraction of coal carbon detected by CP/MAS- ^{13}C -NMR is described in 2.1 along with quantitative measurements of this fraction for a few coals of differing rank and a few chemically modified coals. Section 2.2 presents initial results concerning the regiospecificity of a ^1H - ^{31}P - ^{13}C -DCP/MAS- ^{13}C -NMR technique, which has been gained from model compound studies. Recent developments in the application of strong base chemistry to the investigation of acidic C-H and O-H sites in coals are described in 2.3 and 2.4 including a new controlled pH methodology for studying the distribution of O-H sites in coal with $\text{pK}_a < 12$. The trans-alkylation reaction has been used to probe the aliphatic structure of several coal products and derivatives (2.5), and model compound studies have clarified the origin of some unexpected products. Section 2.6 highlights the major effects of surface immobilization on altering the thermal reaction pathways for bibenzyl and presents initial results on the thermolysis of surface immobilized 1,3-diphenylpropane.

2.1 Quantitative Aspects of Solid State, High Resolution ^{13}C -NMR Spectroscopy of Coals

2.1.1 Spin Counting Experiments Using Coal/Amino Acid Mixtures

(E. W. Hagaman, R. R. Chambers, Jr.,
M. C. Woody)

In a previous report¹ it was established that an upper limit of two thirds of the organic carbon of Ill. No. 6 vitrain derivatives contributes to the observable magnetization in CP/MAS- ^{13}C -NMR spectra. We now report spin counting experiments, appropriate for both native and chemically modified coals, which establish that the actual fraction of organic carbon of Ill. No. 6 vitrain monitored by this spectroscopic technique is $0.55 \pm .05$. We further show that the underrepresentation of the carbon magnetization in coals by this method is a general result.

A CP/MAS- ^{13}C -NMR experiment which measures the "true" fraction of coal that is observable requires that the response of the reference signal be demonstrably quantitative. This can be accomplished by using the integrated intensity of a diamagnetic organic compound as the reference against which the coal spectrum is compared. This general type of experiment is not new; it has been reported, *inter alia*, in the context of coal quantification studies.^{2,3,4} The results of these studies, as a whole, are inconclusive, reaching diametri-

cally opposed conclusions. In most instances these experiments use a diamagnetic organic standard, whose nmr response is measured separately, and then compared with the coal response, measured separately, or are dilution experiments in which varying proportions of coal and standard are consecutively measured. In the latter case, the response of the system is judged by the agreement between measured and predicted changes of f_a . The details of these experiments require that the measurements are not performed under rigorously identical conditions.

The uncertain features of these spin counting procedures can be circumvented in an experiment in which the coal and standard are measured simultaneously as a uniform blend of dry powders. The complete experiment is performed on a single mixture of the two components. This method guarantees that the coal and standard occupy the same volume element and experience the same H_1 r.f. fields and probe sensitivity during the measurement.

The substance used as the standard must be a pure diamagnetic solid that is unreactive with coal as a mixture of dry powders. It should have relaxation time constants that permit quantitative detection of its carbon resonances under conditions appropriate for coal analysis. The substance should have at least one carbon resonance completely resolved from the reso-

nance area of the coal. This feature permits a quantitative assessment of the standard resonance signal, pure, and in the presence of the coal, and allows the ratio analysis to be performed on a single sample.

Glycine is a suitable standard for use with coals that contain little or no ketonic or acid carbonyl functionality. Thioglycine hydrochloride is an acceptable alternative for coals which contain carboxylic acid/ester functionality but little or no ketonic carbonyl carbon. The latter substance is mildly hygroscopic and must be handled accordingly.

Pertinent relaxation time constants for the pure standards are given in Table 2.1. Both display $T_1(H) < 200$ ms and hence will thermally equilibrate fully during the 1 s pulse repetition delay employed in coal analyses. The cross polarization times of the reference carbons should ideally be < 250 μ s for use in single spectrum analysis of coals with $t_{cp} = 1$ ms. The experimental T_{CH} for the carbonyl carbon of thioglycine hydrochloride (360 μ s) and glycine (440 μ s) yield 94 and 90%, respectively, of their theoretical signal intensity in 1 ms, neglecting damping by $T_{1p}(H)$. These time constants are completely satisfactory if relative areas are determined by the multi-spectrum analysis fitting procedure described previously. The $T_{1p}(H)$ values of the standards are unchanged upon admixture with coal. Hence, at the molecular level, the protons of the

standard and coal do not communicate by spin diffusion. This property of the system guarantees a quantitative response for the standard.

From the elemental analyses of the coal and the weights of coal and standard in the sample, the ratio mg C (carbonyl carbon of standard)/mg C (coal) may be computed. This quantity serves as the reference against which the analogously defined nmr ratio: (area of the carbonyl carbon resonance of the standard)/(area of the coal spectrum) is measured. The weight and area ratios determined from several mixtures of Ill. No. 6 vitrain with glycine or thioglycine HCl are collected in Table 2.2. The ratio of these parameters, the last column in Table 2.2, is the evaluation criterion for this experiment. Its value is unity if the nmr area measurements are quantitative. Its actual value, 0.56 ± 0.03 , is the fraction of coal carbons of Ill. No. 6 vitrain which contribute to the observable magnetization in the CP/MAS- ^{13}C -nmr spectrum. The last two entries in Table 2.2 are for Ill. No. 6-OCH₃/glycine and Ill. No. 6-OCH₃-CCH₃/glycine mixtures. The first coal derivative has been methylated at oxygen sites, while the second derivative has also been methylated at primarily doubly benzylic carbon sites. In these samples, the resonance area of the coal (excluding contribution from the introduced methyls) is calculated from the measured aromatic resonance area and f_a of Ill. No. 6 vitrain (0.70). In this fashion, the evaluation criterion monitors the coal carbon of these derivatives and reveals that the fraction of observable coal carbon in the derivatives is indistinguishable, within the error limits, from that of the precursor coal, Ill. No. 6 vitrain.

The data presented in reference 1 can now be renormalized to reflect this fraction of observable coal carbon and to evaluate the fraction of introduced methyl carbons which are actually detected in the nmr spectrum. This result is shown graphically in Fig. 2.1, which summarizes the conclusions of the combined ^{14}C , ^{13}C -double labeling and the spin counting experiments for

Table 2.1. Relaxation Times for Glycine and Thioglycine-HCl

	$T_{1p}(H)$ (ms)	$T_1(H)$ (ms)	$T_{CH}(\text{Carbonyl})$ (μ s)
Glycine	4.2 ± 0.2^a	62 ± 3	440 ± 10
Thioglycine-HCl	5.5 ± 0.1^b	195 ± 5	360 ± 10

^a Measured with a 42 KHz H_1 r.f. field.

^b Measured with a 52 KHz H_1 r.f. field.

Table 2.2. Weight and Area Ratios for Ill. #6 Vitrain/Glycine, Ill. #6 Vitrain/thioglycine-HCl, and Ill. #6 Vitrain Derivative/Glycine Mixtures

	Wgt. ratio ^a mgC (carbonyl,std.) mgC (coal)	nmr ratio ^{b,c} area (carbonyl,std.) area (coal)	Wgt. ratio ^c nmr ratio
Ill. #6/thioglycine-HCl	0.121	0.23 (0.21) ^d	0.53 (0.58) ^d
Ill. #6/thioglycine-HCl	0.118	0.20	0.59
Ill. #6/glycine	0.219	0.40	0.55
Ill. #6-OCH ₃ /glycine	0.184	0.34	0.54
Ill. #6-OCH ₃ -CCH ₃ /glycine	0.183	0.31	0.59

^aError is $\pm 1\%$.

^bSingle spectrum analysis, $t_{cp} = 1$ ms.

^cError is $\pm 10\%$.

^dThese values result from areas determined by fitting $I(t)$ vs t_{cp} data.¹

Fig. 2.1. Fraction of carbon observed in CP/MAS-¹³C NMR

Ill. No. 6 vitrain and its derivatives. Each of the three identifiable carbon subsets, (1) coal carbon, (2) introduced O-methyl carbon, and (3) introduced C-methyl carbon, is substantially underestimated in the nmr spectrum, and detected to a different degree. The similar response of the C-methyl and coal carbon fractions in Ill. No. 6-OCH₃-CCH₃ presents a false sense of quantitation as judged solely by the ¹⁴C, ¹³C-double labeling experiment, unless it can be independently shown that the observable

carbon magnetization is a true reflection of the total organic carbon of the sample. The value of this experiment is in establishing relative response factors. Additional experiments which place one or more of these factors on an absolute carbon basis are required. The easily implemented spin counting experiment described herein serves this purpose.

The underrepresentation of the carbon magnetization in coals appears to be general, as demonstrated in Table 2.3, which summarizes the results of spin counting experiments on three coals of widely differing rank. In each case, a major fraction of the coal carbon is not detected.

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2. D. L. Vanderhart and H. L. Retcofsky, Preprints of the 1976 Coal Chemistry Workshop, August 26-27, 1976, pp. 202-218, Stanford Research Institute, Menlo Park, CA.
3. D. E. Menner, A. Pines, D. D. Whitehurst, Philos. Trans. R. Soc. Lond. Ser. A **300**, 15 (1981).

Table 2.3. Weight and Area Ratios for Coal/Amino Acid Mixtures

	Wgt. ratio ^a mgC (carbonyl, std.) mgC (coal)	nmr ratio ^{b,c} area (carbonyl, std.) area (coal)	Wgt. ratio ^c nmr ratio
Lignite/glycine	0.149	0.25	0.60 ^d
Bituminous coal/ amino acid mixtures	h	h	0.55 ± 0.03 ^f
Anthracite/glycine	0.090 0.103 0.095	0.20 0.20 0.22 ^e 0.21 0.25 ^e	0.44 ± 0.06 ^g
Anthracite/thioglycine-HCl	0.085	0.17	

^aError is ±1%.

^bSingle spectrum analysis, $t_{cp} = 1$ ms.

^cError is ±10%.

^dSingle measurement. Error estimated to be ±10%. The glycine carbonyl resonance is not separated from the acid resonances of the coal. The carbonyl area was defined by subtraction of the mixture spectrum from that of the separately measured lignite spectrum.

^eThese values result from areas determined by fitting $I(t)$ vs t_{cp} data.¹

^fThis error represents the range for the five values given in Table 2.2.

^gThis error represents the range for the six values from anthracite/amino acid mixtures.

^hData in Table 2.2.

4. J. R. Kalman, "Magnetic Resonance. Introduction, Advanced Topics and Applications to Fossil Energy," L. Petrokris and J. P. Fraissard (eds.), D. Reidel Pub. Co., Boston, 1984: NATO ASI Series C, 121, pp. 557-567.

2.1.2 Application of ESR Spectroscopy for Characterizing Coals and Their Derivatives (L. L. Brown, E. W. Hagaman, A. C. Buchanan, III)

As a companion to the studies of coal by ¹³C-NMR techniques, we initiated a study of coal and coal derivatives by electron spin resonance spectroscopy (ESR). The intent of the new investigation is to explore the possible relationship between the known incomplete detection of carbon signals by CP/MAS-¹³C-NMR and the free radical spin abundance in coals which can be determined by ESR.

The ESR measurements require the development of a protocol for data acquisition that measures absolute spin abundances in coal samples with the aid of an authentic reference material.

An ESR spectrometer has been configured for the study of a several milligram size sample of solid, which can be reproducibly positioned in the microwave cavity. The spectrometer operates at a nominal microwave frequency of 9.10 GHz and a magnetic field strength of 3.2 KG. The signal output is collected and stored digitally by means of a signal averager into a Nicolet NIC-80 data processor. The development of absolute spin assay requires the coal sample and reference material be placed in equivalent positions in the microwave cavity and have a small sample volume.¹ Furthermore it is advantageous to match the coal sample with a reference material that has a comparable spin abundance as well as comparable ESR line shape

and line width. Coal is generally found to be in the 1×10^{19} spins g^{-1} range,² and we have observed for an Ill. No. 6 bituminous coal a broad single line ESR spectrum with a peak-to-peak line width of 6.2 G and a spectral width of 44 G. A standard organic free radical of molecular weight $\sim 200 \text{ g mol}^{-1}$ will have a spin abundance of 3×10^{21} spins g^{-1} . Since an optimum coal sample size to fit our data acquisition/processing operation is $\sim 5 \text{ mg}$, the amount of reference material needed for a comparable spin abundance would be only $\sim 16 \text{ } \mu\text{g}$. Preliminary results indicate that the use of solid solutions of a reference standard in bibenzyl (m.p. = 55°C) made by serial dilutions of accurately weighed components will meet the appropriate requirements for a reference material. The stable free radicals under current investigation are 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) and 2,2-diphenyl-1-picrylhydrazyl (DPPH).

1. J. E. Hertz and J. R. Bolton, "Electron Spin Resonance: Elementary Theory and Practical Applications," McGraw-Hill: New York, 1972, pp. 462-464.
2. H. L. Retcofsky, J. M. Stark, and R. A. Friedel, *Anal. Chem.* **40**, 1699 (1968).

2.2 ^1H - ^{31}P - ^{13}C DCP/MAS NMR of Organophosphorus Compounds

(E. W. Hagaman, R. R. Chambers, Jr., R. L. Rardin¹)

The information content of ^1H - ^{31}P - ^{13}C -double cross polarization and magic angle spinning (DCP/MAS) NMR spectra is that of the simpler ^{31}P - ^{13}C CP/MAS experiment performed with ^1H dipolar decoupling. The initial ^1H - ^{31}P polarization transfer step allows the repetition rate of the experiment to be determined by the typically shorter ^1H T_1 rather than the ^{31}P (or ^{13}C) T_1 . The relative magnitude of these spin lattice relaxation times is given in Table 2.4 for several related phosphonylfluorene derivatives.

The ^{31}P - ^{13}C CP transfer step requires that both the ^{31}P and ^{13}C $T_{1\rho}$, i.e., the spin lattice relaxation time in the rotating field, be

Table 2.4. Relaxation Times of 9-Phosphonylfluorene Derivatives

	R=CH ₃ , R'=CH ₃	R=Ph, R'=CH ₃
^1H $T_1(\text{s})^a$	0.95	3.6
^{31}P $T_1(\text{s})$	26.0	54
^{13}C $T_1(\text{s})$		
(147 ppm)	37 ± 2	
(140 ppm)	43 ± 2	
(130 ppm)	53 ± 6	
(120 ppm)	50 ± 5	
(53 ppm)	26 ± 4	
^{31}P $T_{1\rho}(\text{ms})$	29 ± 1^b 11.9 ± 0.5^c	
^{13}C $T_{1\rho}(\text{ms})$		
(147 ppm)	120 ± 20	
(130 ppm)	33 ± 2	

^aFor R=CH₃, R'=Ph and R=R'=Ph, the ^1H T_1 values are 1.4 and 12.4 s respectively.

^b25 KHz r.f. field.

^c20 KHz r.f. field.

long compared to the experimental transfer time, which for these examples is 4 ms. The $T_{1\rho}$ values given in Table 2.4 span the range 12-120 ms and satisfy this condition. The strong r.f. field dependence found for the ^{31}P $T_{1\rho}$ of 9-dimethylphosphonyl-9-methylfluorene indicates the importance of conducting the experiment with the largest possible spin locking r.f. fields.

The DCP/MAS- ^{13}C -NMR spectrum of di-*o*-anisylphosphine oxide (aromatic region) is compared in Fig. 2.2 with the standard ^1H - ^{13}C CP/MAS- ^{13}C -NMR spectrum. While the latter spectrum has resonances for each carbon in the sample, the DCP spectrum contains signals for only those carbons one and two bonds removed

from the phosphorus atom, i.e., those carbon centers within ca. 3 Å of the phosphorus atom. It is interesting to note that the areas for the C(2) and C(6) resonances in the DCP spectrum (Fig. 2.2.), which should be equal on the basis of the atomic ratio, are actually in the ratio $e^{-\gamma_{CT}/T_{1\rho}C(2)}/e^{-\gamma_{CT}/T_{1\rho}C(6)}$. This further demonstrates the need to use large spin locking r.f. fields to make $T_{1\rho}$ as long as possible. However, it is clear that the appli-

Fig. 2.2. Comparison of DCP/MAS and CP/MAS- ^{13}C -NMR spectra for di-o-anisylphosphine oxide.

cation of this ^1H - ^{31}P - ^{13}C DCP/MAS NMR technique to a selectively ^{31}P -labelled coal derivative has the potential of providing specific structural information on carbon nuclei in the immediate vicinity of the introduced phosphorus nuclei.

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2.3 Tetraalkylammonium Hydroxide - Promoted Methylation of Illinois No. 6 Vitrain

(R. R. Chambers, Jr., E. W. Hagaman, M. C. Moody)

The base-promoted alkylation of coal using a strong base and an alkyl halide represents a powerful technique for analyzing the acidic sites in coal. When the alkyl halide is C-13 and C-14 double labeled, the extent of reaction can be quantified using the C-14 label and the reactive sites identified by solid-state ^{13}C NMR.¹

The treatment of oxygen-rich coals with a tetraalkylammonium hydroxide base followed by reaction with an alkyl halide has become a standard procedure for characterizing the phenolic and carboxylic acid components in coal.² Under the experimental conditions, phenols are converted to aryl-alkyl ethers and carboxylic acids to the corresponding alkyl esters. Based on an infrared analysis of the coal product, it has been suggested that all of the acidic -OH sites are derivatized during a single, two-step treatment.³ In order to improve our understanding of this reaction as well as to identify the reactive sites in coal, we probed the alkylation of a bituminous coal by this reaction sequence. The important findings of this study are: (1) multiple treatments are necessary to achieve exhaustive alkylation, even when the coal is reacted for extended time periods with a large excess of reagents, and (2) structural units in coal which contain acidic C-H sites, such as fluorene, are also susceptible to alkylation under appropriate conditions.

The coal chosen for study was a vitrinite-rich ill. No. 6 sample for which the distribution of acidic C-H sites has already been established.¹ The coal was neutralized for a pre-determined length of time (1 h or 68 h) with an excess of tetrabutylammonium hydroxide dissolved in an aqueous tetrahydrofuran (THF) medium (0.27 M in base, 73 mole % THF, 27 mole % H_2O , 9.5 mmoles base/g coal), and the reaction terminated by adding an excess of C-13,

C-14 double labeled methyl iodide (28.6 μ moles/g coal). The alkylation reaction was allowed to proceed for 1 week. Since the reaction of methyl iodide with the base is complete in 2 days, this length of time is sufficient to insure complete methylation of the anionic sites generated on coal during the neutralization step. After workup, the extent of reaction, expressed as the number of $^{14}\text{CH}_3$ groups per 100 coal carbons, was determined by radioassay of the coal product. In each case, the final calculation assumes that 5% by weight tetrabutylammonium salt is retained by the coal based on earlier measurements. The isolated product was then subjected to methylation again by an identical procedure. This was continued until no more methyl groups were introduced (4-5 treatments).

The results from the 1 h and 68 h neutralization period are depicted in Table 2.5. An important observation emerges from the data: the coal sample is only partially methylated after the initial two-step treatment when a 1 h neutralization period is used. Furthermore, extending the neutralization period to 68 h has virtually no effect, within the experimental error, on either the initial or total extent of methylation. Multiple treatments are still required to achieve exhaustive methylation.

Table 2.5. Exhaustive Alkylation of Illinois No. 6 using $n\text{-Bu}_4\text{NOH}$ and $^{13,14}\text{CH}_3\text{I}$

Treatment No.	No. $^{14}\text{CH}_3$ /100 Coal C	
	Neutralization Time	
	1 h	68 h
1	5.7 ± 0.3	5.3 ± 0.3
2	6.3 ± 0.3	6.7 ± 0.3
3	7.2 ± 0.4	7.2 ± 0.4
4	7.2 ± 0.4	7.8 ± 0.4
5	—	7.9 ± 0.4

Structural information on the reactive sites in this coal was obtained by treating the initial alkylation product from the 1 h neutrali-

zation period with tetrabutylammonium hydroxide followed by acidification. It was found that 0.84 $^{14}\text{CH}_3$ /100 coal C are lost from the 5.7 $^{14}\text{CH}_3$ /100 coal C which were introduced. The solution phase from the reaction mixture was analyzed on a GC equipped with a radioactivity monitor and was found to contain $^{14}\text{CH}_3\text{OH}$. This result suggests that methyl esters are important products of the initial alkylation.

The other product from the hydrolysis of a methyl ester is the tetrabutylammonium salt of a carboxylic acid. Under the conditions of the serial methylation treatments, these carboxylate salts will re-methylate during each methyl iodide quench. Since all of the serial treatments are carried out with methyl iodide at the same isotopic enrichment, this hydrolysis and re-methylation sequence cannot account for the significant increases in added methyl groups which are observed upon repetitive methylation. Instead, the data requires methylation of new anionic sites to occur during each serial treatment.

Further characterization of the reactive sites was accomplished by a combination of spectroscopic and chemical means. A series of difference CP/MAS ^{13}C NMR spectra were collected using the parent coal and the four coal products obtained from the 1 h neutralization. These difference spectra correspond to 1-Parent, 2-1, 3-2, and 4-3, where the numbers refer to the treatment number. The criterion used in making the difference spectra was the nulling of the aromatic-carbon envelopes. Qualitatively, the spectra are consistent with methylation occurring at both oxygen (50-50 ppm) and carbon (<50 ppm) sites during each treatment. On the other hand, a quantitative analysis shows that the oxygen to carbon ratio decreases dramatically with each serial treatment. To illustrate, the O/C ratio from the initial treatment is 75/25 while that same ratio has changed to 40/60 after the third treatment. In other words, the relative amount of oxygen alkylation decreases with each treatment whereas the relative amount of carbon alkylation increases. This shows that the

reaction actually becomes more selective for the C-H sites as the number of treatments increases.

From the NMR analysis and the previous carbon-14 results, it is clear that the initial treatment severely underestimates the total number of alkylatable sites in this coal. Consequently, statistical coal structures which are based on the results from a single alkylation treatment must be regarded as only approximate.

The identity of the reactive C-H sites was clarified by treating the 68 h exhaustive methylation product (7.9/100 coal C) with fluorenyllithium and $^{13,14}\text{CH}_3\text{I}$.¹ We find that this coal derivative is resistant towards methylation under these conditions. In contrast, previous work¹ demonstrated that approximately 2 $^{13,14}\text{CH}_3$ groups per 100 coal carbons can be introduced at carbon sites into an O-methyl Ill. No. 6 sample which had undergone only one treatment with $n\text{-Bu}_4\text{NOH}$ and methyl iodide. Hence, we suggest that fluorene-like structures are also ionized and methylated under the exhaustive $n\text{-Bu}_4\text{NOH}$ -promoted alkylation conditions reported here. This would indicate, as suspected, that hydroxide is a stronger base in a primarily organic medium than in a pure aqueous medium.

The requirement for multiple treatments to fully methylate this coal represents an important property of this reaction. Some factors that might contribute to this phenomenon can be offered. First, the neutralization of acidic sites in coal by a base is a reversible reaction. The degree of ionization will depend upon the relative pH of the base solution and the pK_a of the reactive groups. When methyl iodide is introduced, two competing reactions occur which can have different rates. The anionic sites will methylate to produce the alkylated coal product, and methyl iodide will undergo hydrolysis to form methanol. If hydrolysis is faster than methylation, then only partial alkylation will be achieved because of a shift in pH away from the ionized form of the

coal. Another possibility is that coal may contain structural elements with multiple acidic sites such as dihydroxybenzene or fluorene. If alkylation of these structures occur stepwise, then multiple treatments will be required to achieve exhaustive methylation.

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2. R. Liotta and G. Brons, *J. Amer. Chem. Soc.* **103**, 1735-1742 (1981).
3. R. Liotta, K. Rose and E. Hippo, *J. Org. Chem.* **46**, 277-283 (1981).

2.4 pH-Controlled Methylation of Illinois No. 6 Vitrinite: The Distribution of Acidic OH Sites in Coal

(R. R. Chambers, Jr., M. C. Woody)

Earlier studies of the alkylation of acidic C-H sites in coal by reaction with a strong base and an alkyl halide demonstrated that this process is base strength dependent.¹ By systematically varying the base, the reaction sites in coal could be characterized on the basis of their ionization constant or pK_a value. This information on the activity of the reactive sites greatly facilitated the identification of the structural units which were ionized and subsequently alkylated by the alkyl halide.

A key step in the identification of acidic C-H sites is the initial alkylation of the indigenous heteroatoms in coal. This was accomplished using the phase-transfer, base-promoted alkylation reaction first reported by Liotta.² Since the pH of the base solution is poorly defined, important structural information such as the pK_a of the acidic sites is obscured. Taking a conceptual approach similar to the one described for analyzing the C-H sites, we have undertaken a study to fully characterize these heteroatom sites by methylation at well-defined pH's. Some initial results from this work are presented here.

The coal used for this initial investigation was a vitrinite-rich Ill. No. 6 sample of empir-

ical formula $C_{106}H_{88}M_{2.1}O_{12}S_{1.0}$. The sample was neutralized with an excess of tetrabutylammonium hydroxide in an aqueous hydrofuran medium (1 g coal, 3 ml THF, 10.6 mmoles base). After 16 h, water was added to the sample and the pH monitored with a glass electrode. A partial titration curve for acidification of the sample was obtained by adding standard HCl from a burette. Equilibration of this heterogeneous mixture after each acid addition was typically a slow process. Several hours were allowed for the sample to reach equilibrium. The base capacity of the coal as a function of pH was calculated as the difference between the amount of base added initially and the amount of added acid. In this analysis, the base capacity represents the sum of the amount of base neutralized by acidic sites on the coal, or charge density, and the amount of chemisorbed base.

An excess of C-13, C-14 enriched dimethyl sulfate, $(CH_3)_2SO_4$, was added to the coal sample.³ The pH of the reaction was maintained constant for 2 h by slow addition of dilute $n\text{-Bu}_4\text{NOH}$ from a burette. The number of alkylated sites was then determined by combustion analysis. Additional structural information on the identity of the methylated sites was obtained by base hydrolysis ($n\text{-Bu}_4\text{NOH}$) of the methylated coal samples. The number of base labile methyl groups was established by carbon-14 counting. The titration results along with the corresponding C-14 data are shown in Table 2.6.

The following observations emerge from this preliminary data. First, the base capacities as measured by titration and the C-14 methylation results are both pH dependent, each increasing with an increase in the solution pH. And secondly, the total number of introduced ^{14}C groups is identical, within experimental error, to the base capacity measurement. For these reasons, we conclude the base capacities represent the actual charge density on the coal and that complete methylation of these anionic sites has been achieved. A significant degree of ionization (1.4/100 coal C) is apparent at pH values as low as 7. The titration of 'model

Table 2.6. pH-Controlled Ionization and Methylation of Illinois No. 6

pH	Base Capacity ^a (No./100 Coal C)	No. $^{14}CH_3$ /100 Coal C ^b	
		Total	Base Labile
12	3.5 ± 0.2	—	—
7.3	1.3 ± 0.4	1.37 ± 0.01	0.90 ± 0.01
5	—	0.90 ± 0.08	0.68 ± 0.05
2	0.3 ± 0.3	0.18	>0.12

^aThe average of 3-4 determinations.

^bThe average of 2-3 determinations.

compounds' indicates that acidic sites with $pK_a < 7$ will ionize at pH's less than or equal to 7. Assuming these sites to be -OH groups, the data is consistent with structural elements such as carboxylic acids ($RCOOH$) and vinylogous acids ($RC(O)-CH=CH-OH$). The methylation of carboxylic acids under these conditions will produce methyl esters which are susceptible to base hydrolysis. The C-14 base hydrolysis data can thus be taken as additional support for ionization and methylation of carboxylic acids under these conditions.

1. R. R. Chambers, Jr., E. W. Hagaman, M. C. Woody, K. E. Smith, and D. R. McKamey, *Fuel* **64**, 1349-1354 (1985).
2. R. Liotta and G. Brons, *J. Amer. Chem. Soc.* **103**, 1735-1742 (1981).
3. Carbon-14 dimethyl sulfate was obtained by the reaction of $^{14}CH_3OH$ with chlorosulfonic acid, $ClSO_3H$. This product was combined with commercially available Carbon-13 enriched dimethyl sulfate.

2.5 Studies of Coal Structure by Acid Catalyzed Transalkylation

2.5.1 New Chemical Structural Features of Coal. The Structure of Coal Derivatives (B. M. Benjamin, E. C. Douglas)

Previous work in this series was concerned with the identification of the various chemical

species arising from the transalkylation reaction on coals¹ and the use of the reaction to compare concentrations of these species in coals of different ranks.² We now report our results of the transalkylation reaction on the following materials derived from coals: (1) the pyridine soluble and insoluble parts of Kentucky No. 9 (PSOC-213) and Illinois No. 6 coals, (2) an SRC derived from Kentucky No. 9 coal, (3) a Birch reduced Illinois No. 6 coal, (4) an O-methylated Illinois No. 6 coal, and (5) coke derived from Illinois No. 6 coal.

In our version of the transalkylation reaction, trifluoromethanesulfonic acid (TFMSA) is used as catalyst and toluene as acceptor. The general procedure and reaction conditions were described earlier.² Pyridine extractions were done in a Soxhlet apparatus. Illinois #6 coal was 14% extractable and Kentucky #9 was 13% extractable. The pyridine extracts were thoroughly washed with 5% THF in water³ followed by hot water to remove adsorbed pyridine. Careful attention was given to this step to assure that added acid catalyst would not be neutralized and that acid concentrations would be comparable to those in other experiments.

Careful attention was also given to the step in which the insoluble residue was washed after each reaction cycle. Reactions were quenched by the addition of sodium bicarbonate and water after which a measured quantity of triphenylmethane was added for a gc integration reference. Before going to the next reaction cycle, it was necessary to completely remove excess sodium bicarbonate by repeated water washes. All soluble organic matter was next removed by thoroughly washing the residue with hexane. We noted on some occasions, particularly with Kentucky #9 fractions, that some organic molecules such as methyltolynaphthalenes, tritolylmethanes, and triphenylmethanes were difficult to remove with the hexane wash. This may have been due to adsorption in pores just the right size to hold the molecules. Also the problem may have been due to difficulty in wetting the residue with hexane after it was washed with water. It is

absolutely necessary to remove triphenylmethane because it will appear in the next step in the form of excess tritolylmethane. The problem was rectified by first drying the samples and then washing them a second time with a small quantity of toluene followed by hexane.

Pyridine Soluble and Pyridine Insoluble Parts. Data for transalkylation reactions on the pyridine soluble and insoluble parts of Kentucky #9 and Illinois #6 coals are recorded in Table 2.7. We showed earlier¹ that a collection of aliphatic substituents are transferred to toluene. Included among these substituents are pendant aliphatic chains, methylene connecting groups, and methine crosslinking groups. Inspection of the table shows that the pyridine soluble fractions are richer in aliphatics than the pyridine insoluble fractions, a total of 1.9 vs 1.6 per 100 carbon atoms in Kentucky #9 coal and 1.7 vs 1.4 in Illinois #6 coal, respectively.

Whereas a large difference is seen in the concentration of ethyl and other alkyl groups, only a small difference is seen in the concentration of methylene connecting groups. Conversely, the methine group is considerably more abundant in the pyridine insoluble part, a comforting observation which reflects the higher degree of crosslinking considered to be related to the insoluble nature of that fraction. Concentrations of excised aromatics show no particular trends. Thus the structural features of the soluble and insoluble parts of these two coals differ, but they differ more in the quantity of substituents than they do in the nature of the substituents. Hence from the viewpoint of the transalkylation reaction, the two parts of the coals investigated here look somewhat alike structurally except for the size and degree of crosslinking of the molecular clusters and their degree of substitution.

Modified Coals. O-Methylated Illinois #6 coal was prepared by a method similar to that described by Liotta.⁴ This coal was then subjected to transalkylation. Analysis of the reaction product gave results very similar to those obtained for the parent coal.² The only

Table 2.7 Numbers of Groups per 100 Carbon Atoms in Four Cycles of Transalkylation

Compound Isolated	Ky. No. 9		Ill. No. 6		
	Py. Sol.	Py. Insol.	Py. Sol.	Py. Insol.	Birch Reduced
Ethyltoluene	0.25	0.10	0.32	0.17	0.14
Propyltoluene	0.16	0.076	0.16	0.10	0.085
Butyltoluene	0.064	0.027	0.050	0.036	0.029
Pentyltoluene	0.012	0.009	0.008	0.008	0.009
Phenyltolylmethane	0.026	0.060	0.029	0.043	0.030
Ditolylmethane	0.95	0.85	0.83	0.76	0.70
1,1-Ditolylethane	0.12	0.22	0.10	0.15	0.18
1,2-Ditolylethane	0.038	0.022	0.031	0.022	0.072
1,1-Ditolylpropane	0.045	0.044	0.025	0.035	0.036
1,2-Ditolylpropane	0.067	0.026	0.037	0.017	0.012
1,1-Ditolylpropene	0.022	0.004	0.030	0.014	0.017
1,1-Ditolylbutane	0.020	0.008	0.027	0.012	0.010
Tritolylmethane	0.048	0.15	0.010	0.026	0.020
1,1,2-Tritolylethane	0.050	0.056	0.012	0.035	0.069
1,1,3-Tritolylpropene	0.018	0.027	0.012	0.028	0.026
Naphthalene	0.009	0.006	0.007	0.005	0.004
Methylnaphthalene	0.057	0.069	0.040	0.039	0.033
Dimethylnaphthalene	0.047	0.039	0.038	0.029	0.016
Trimethylnaphthalene	0.016	0.008	0.012	0.008	0.006
Methyltolynaphthalene	0.063	0.069	0.061	0.090	0.015
Total Aliphatics	1.9	1.6	1.7	1.4	1.3
Total Aromatics	0.20	0.20	0.16	0.17	0.074

noticeable differences were a slight lowering in the number of ethyl and propyl groups transferred. This difference could indicate the occurrence of some base catalyzed cleavage of labile ethers or esters in the coal as a result of the O-methylation procedure. Therefore it appears that O-methylation does not seriously change the basic structure of coal. A similar result was obtained from a sample of air oxidized coal which was prepared by drawing air through wet coal for two weeks. Products from the transalkylation reaction on this derivative were again similar to the parent coal.

On the other hand, significant changes are effected by Birch reduction⁵ of the same coal. Noticeable differences occur in the numbers of excisable groups, Table 2.7. For example, after reduction of the coal, fewer ethyl groups can be transferred to toluene, 0.14 per 100 carbons in the reduced coal as compared to 0.32 in the untreated coal. The quantities of methyl substituted naphthalenes released from

the reduced coal are about a third lower than those from the original coal. These results probably reflect the preferential reduction of the aliphatic substituted rings of the polynuclear aromatic clusters. An increase in the amount of 1,2-ditolylethane (indicative of the dimethylene unit) is believed to result from adsorbed reagent, glyme or triglyme used in the Birch reduction, as demonstrated by model experiments to which triglyme was added.

SRC. A sample of SRC derived from Kentucky #9 coal⁶ was treated in the usual way with TFMSA and toluene. The SRC appeared to be about half soluble in the toluene, and after the first cycle of transalkylation, only 46% of the starting material remained as insoluble residue. For this reason, results from only the first cycle are recorded. The capillary gc trace of the reaction product was rich in peaks and completely different from that of the starting SRC. The gc/ms revealed a large variety of substituted tetralins, indanes, phe-

nanthrenes, fluorenes, pyrenes and other aromatics (Table 2.8). The only major component common to both SRC and transalkylated SRC was phenanthrene, and its concentration was nearly the same in both. Other common aromatic components which occurred in very minor amounts were methylnaphthalene, biphenyl, diphenyl ether, dimethylnaphthalene, methylphenanthrene, pyrene, and methyl dihydropyrene. The occurrence of small amounts of biphenyl and diphenyl ether might be traced to leaks in the Dowtherm heat exchanger of the SRC process. This problem was encountered in the analysis of certain recycle solvents.

Most of the starting SRC could not be analyzed by capillary gc and gc/ms because the molecular weights of the components were too great. Less than 10% of the material appeared as gc peaks. While the SRC has a very high boiling point, its transalkylation products are more volatile. More than half of the toluene soluble material passes through the gc. A partial list of the components and their concentrations is given in Table 2.8. The list is divided into two parts. For convenience in making comparisons, the first part of the list is comprised of the same materials cleaved from

the parent coal. These, in general, are the major components.

The most noticeable aspects of these data are (1) the low concentration of methylene connecting groups in the SRC as evidenced by ditolylmethane, and (2) the near absence of the methine crosslinking group as evidenced by the very low concentration of tritolylmethane. Pendant alkyl substituents are surprisingly present in the SRC. In fact, chains up to 14 carbons in length were found, although in low concentration. Thus the list of products shows that thermolysis in the presence of an H-donor eliminates or modifies many of the connecting groups while having only moderate effect on the alkyl substituents. In addition, transalkylation of SRC results in the excision or formation of a large variety of aromatics, hydroaromatics, and their methyl derivatives and also releases a small amount of benzene (not produced from coal). These results suggest that the liquefaction process extensively disrupts the polynuclear aromatic clusters producing molecular fragments which are not necessarily present in the parent coal.

Coke. It is expected that pyrolysis reactions which occur at the high temperatures,

Table 2.8. Products From One Transalkylation Cycle of SRC and Ky. #9 Coal in Numbers of Groups per 100 Carbon Atoms

Compound Isolated	SRC	Parent Coal	Compound Isolated	SRC	Parent Coal
Ethyltoluene	0.17	0.14	Naphthalene	0.0090	tr
Propyltoluene	0.062	0.076	Methylnaphthalene	0.012	0.031
Butyltoluene	0.021	0.019	Dimethylnaphthalene	0.0073	0.012
Pentyltoluene	0.012	0.0072	Trimethylnaphthalene	tr	0.0042
Phenyltolylmethane	0.0041	0.013	Methyltolylmethane	tr	0.0059
Ditolylmethane	0.20	0.51			
1,1-Ditolylethane	0.0089	0.088			
1,2-Ditolylethane	0.0040	0.012	Indane-C-2, -C-3, -C-4	0.017	0.0035
1,1-Ditolylpropane	0.0047	0.028	Tetralin-C-1, -C-2, -C-3, -C-4	0.012	0.002
1,2-Ditolylpropane	tr	0.0061	Fluorene, -C-1, -C-2, -C-3	0.017	tr
1,1-Ditolylpropene	0.013	0.019	Phenanthrene, -C-1, -C-2, -C-3	0.020	tr
1,1-Ditolylbutane	tr	tr	Fluoranthrene, -C-1, -C-2	0.035	—
Tritolylmethane	0.0020	0.026	Pyrene, -C-1, -C-2	0.035	—
1,1,2-Tritolylethane	—	0.023	Biphenyl, -C-1, -C-2, -C-3, -C-4	(a)	—
1,1,3-Tritolylpropene	tr	0.019	Dibenzofuran, -C-1, -C-2	(a)	tr
			Chrysene, -C-1, -C-2	(a)	—
			Binaphthyl, -C-1, -C-2	(a)	—

^aConcentrations were not estimated because of overlap of gc peaks.

800-900°C, necessary for coke preparation⁷ would so modify coal structure that its original features could not be recognized through any diagnostic chemical reaction. Many of the features such as methylene connecting groups and practically all of the pendant alkyl substituents will have been ruptured and will have escaped with the tar or gas. The transalkylation reaction reveals that the residual coke contains almost no alkyl functions and that the aromatic units can not be split out of the remaining network. Only very small amounts of ethyl, propyl, and methylene were present (0.010, 0.0023, and 0.012 per 100 C atoms respectively) along with several isomers of a substance with molecular weight 214 (0.0096 per 100 C atoms). Although this compound has not yet been characterized and has not been detected in model compound studies, it is believed to contain 14 carbon atoms, including a methyl group and an oxygen atom. We have recognized that this compound is found in small quantities in the transalkylation products of some coals.

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6. The material referred to as SRC is filtered SRC T102 bottoms, run No. 72, L125, date 4/19/76, SN No. 74690, supplied by W. H. Webber, EPRI.

7. Coke was prepared by heating powdered Illinois #6 coal in a quartz tube to 800°C for 1 hour in a stream of argon.

2.5.2 Studies of Model Systems: The Possible Origin of Some Unusual Compounds

(B. M. Benjamin, E. C. Douglas)

The work described in this report deals primarily with experiments on a limited group of model compounds which resemble coal partial structures. We are interested in their response to acid catalysis under conditions similar to transalkylation of coals. These experiments are aimed at understanding the origin of a particular group of compounds derived from coal under the same conditions. The chemical derivation of this group of compounds has been difficult to rationalize.

The origin of a group of substituted tetralins and indanes (mol. wt. = 188 and 202), several isomers of methyltolynaphthalene (mol. wt. = 232), and several isomers of 1,1,2-tritolylethane (mol. wt. = 300) will be examined first. Based on model experiments, we believe that at least part of these compounds are derived from reactions of polynuclear aromatics, and supporting evidence is set forth in the following paragraphs.

In previous work¹ it was necessary to demonstrate that alkyl groups transferred more rapidly from polynuclear aromatics than from monocyclic aromatics. While attempting to study the relative rates of ethyl transfer from benzene as compared with certain polycyclic aromatics, we noted that the product mixture frequently contained small amounts of numerous compounds. In several experiments, the gc/ms analysis of the products revealed the presence of molecules with molecular weights of 188, 202, and 232, and the cracking patterns of these molecules in the mass spectra were similar to those for compounds derived from coal. Suggested structures for the substituted indanes and tetralins based on the ms cracking patterns are portrayed in Fig 2.3. These observations suggest that the polynuclear aromatic part of the substrate molecules entered extensively into reactions when catalyzed by

ORNL DMG 85-18568

Fig. 2.3. Structures of substituted tetralins and indanes derived from coal.

acids. The observations also imply that some of the compounds derived from the transalkylation of coal may arise from reactions of the aromatic components of the coal polymer network.

Previously, experiments designed to study transalkylation reactions only made use of simple substituted monocyclic aromatics. The monocyclic compounds are quite stable, and aromatic breakdown was not observed. It does not appear that the more complicated substituted polynuclear aromatic (PNA) systems have been studied, and it is not known how they behave during alkyl transfer. Therefore we undertook a study of the reactions of a limited selection of PNA's under conditions similar to those used with coal. The unsubstituted and methyl substituted PNA's were found to react to produce varying amounts of products depending on structure. A summary of the results are presented. Reaction conditions were as follows: a mixture of 0.20 g of reactant, 10 ml of toluene, and 0.2 ml of trifluoromethanesulfonic acid were refluxed for 6 h. The acid was neutralized with bicarbonate solution, an integration reference was added, and the organic layer was analyzed by gc and gc/ms.

Anthracene reacted nearly completely. Only 1.9% of the starting material was recovered, and more than 200 products were found by capillary gc. The main product, tetrahydroanthracene, was present at only 0.13 mole percent, and all other materials were present in

smaller amounts. Nonvolatile higher molecular weight materials were formed from more than half of the starting anthracene. The same product distribution was formed from 9,10-dihydroanthracene which is probably an intermediate in the reaction. For the purposes of this discussion, the pertinent part of the data involves those compounds with molecular weights of 188, 202, and 232. The materials with molecular weights of 188 and 202 will be considered first. In the mass spectrometer, they crack to give ions with $m/z = 118, 130, 131, 145,$ and 187 , typical of methyl and butyl fragment loss from substituted indanes, tetralins, methylindanes, and methyltetralins.

Methylphenanthrene and pyrene are not as reactive as anthracene. About 90% of the starting materials were recovered, but the product slate in both cases included materials with molecular weights 188 and 202, the same materials as found from anthracene. These compounds have also been observed as products resulting from acid treatment of a large variety of PNA's such as 9-ethylphenanthrene, 1,2-bis-(9-phenanthryl)-ethane, 1-ethylpyrene, chrysene, triphenylene, perylene, and 1,2-benzfluorene. A suggested reaction scheme is presented in Fig. 2.4 for the formation of methylbutyltetralin from a substituted phenanthrene moiety in coal.

A group of compounds with molecular weight 232 are found in the products of transalkylation of most coals. The compounds are isomeric and all have similar mass spectral cracking patterns. Their structures were established by comparison with the ms cracking patterns of an authentic sample of methyltolynaphthalene. It seems possible that several isomers of methyltolynaphthalene can be formed directly from methylnaphthalene (itself an abundant product from coal) prior to, or after it is cleaved from coal. Furthermore, several isomers of the compound are found when 1- or 2-methylnaphthalene is treated with acid in toluene solution. However the simplest route, that is, starting from methylnaphthalene, is not the only source of methyltolynaphthalene.

ORNL-DWG. 85-18567

Fig. 2.4. Possible reaction sequence resulting in methylbutyltetralin.

Compounds with molecular weights of 232 are also derived in trace amounts from acid treatment of anthracene as well as from chrysene and certain substituted pyrene and phenanthrenes, although methyltolynaphthalenes are not formed from unsubstituted pyrene and phenanthrene nor from 3-methyl and 1-methylphenanthrene.

Numerous isomers of 1,1,2-tritolylethane are found in coal transalkylation mixtures. We earlier proposed² that these compounds are derived partially from trisubstituted ethanes in the coal network. We have now found that another source of 1,1,2-tritolylethane exists. It can result from the acid treatment of certain substituted phenanthrenes. The reaction of 3-methylphenanthrene in toluene gave several isomers of 1,1,2-tritolylethane, and from studies of 1-methylphenanthrene, it was shown by carbon-14 labeling that the ethyl moiety is derived from the 9,10-positions. A possible reaction scheme is presented in Fig. 2.5.

The last group of unexpected transalkylation products considered here are derivatives of propene (mol. wt. 222, 236, 312 and 326). The compounds (1,1-ditolylpropenes and 1,1,3-tritolylpropenes) were identified by comparison of their mass spectra with authentic samples. We tentatively propose that a portion of these compounds are derived from lignin-like

ORNL-DWG. 85-15098

Fig. 2.5. Reaction scheme for the formation of 1,1,2-tritolylethane from the reaction of 3-methylphenanthrene with TFMSA in toluene.

structures or residues in coal which originate from lignin. This possibility is supported by the fact that the compounds are produced in small amounts by the transalkylation of a pine lignin. A simplified structure for lignin is represented in Fig. 2.6. Lignin is a polymer of coniferyl alcohol, a hydroxy methoxy derivative of cinnamyl alcohol. When cinnamyl alcohol was treated with TFMSA in toluene, the product mixture contained isomers of 1-phenyl-1-tolylpropene, 1,1-ditolylpropene, and traces of 1,1,3-tritolylpropene.

The possibility that these compounds may have been derived from tetralin or methyl tetralin by the addition of one or two tolyl groups was investigated and ruled out. 1-Tolyltetralin was synthesized and its mass spectrum determined. The cracking pattern was different from

ORNL DMC 85-10549

Fig. 2.6. Structure of lignin and model precursors.

that observed for 1,1-ditolylpropene. In addition naphthalene and the two isomers of methylnaphthalene were treated with TFMSA in toluene. Naphthalene is almost unreactive under the conditions, and 95% of the starting material is recovered. The product mixture included reduced materials resulting from hydride abstraction as well as heavier condensed materials. Small amounts of tolyltetralins, mass 222, and ditolyltetralins, mass 312, were formed. However, their ms cracking patterns were different from those of compounds with the same molecular weights (ditolylpropene and tritolylpropene respectively) derived from coal. The methylnaphthalenes reacted similarly to unsubstituted naphthalene, and the list of products obtained from 2-methylnaphthalene included isomeric methyltolyltetralins, mass 236, which gave ms cracking patterns unlike the compounds with mass 236 derived from coal. No compounds with molecular weight 312 were found but methylditolyltetralins, molecular weight 326, were produced in trace quantities. Again the cracking patterns were different from the products derived from coal. Hence, all evidence indicates that the transalkylation products with mol. wt. 222, 236, 312, and 326 are indeed derivatives of propene.

From the above information we conclude the following: The main products of transalkylation of coal result from rupture of the polymer network and transfer of aliphatic fragments to the solvent, while a variety of aromatics are

released as solutes. Concurrently slower reactions take place in which certain aromatics bound to coal are attacked. These reactions, which involve protonation-deprotonation, hydride transfers, and additions to solvent result in extensive modification of the aromatics attacked. Characteristic derivatives are produced in small quantities. In many cases these compounds may supplement yields of molecules which are merely cleaved from the polymer network. In order to sort out the important contributions of these reactions, a better knowledge of the reactions of aromatics and polynuclear aromatics under the reaction conditions is needed.

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2.6 Effects of Immobilization on the Thermolysis of Surface Attached α,ω -Diphenylalkanes

2.6.1 Surface Immobilized Bibenzyl

(T. D. J. Dunstan,¹ A. C. Buchanan, III, M. L. Poutsma)

The thermal decomposition of α,ω -diphenylalkanes, $C_6H_5(CH_2)_nC_6H_5$, covalently bound to the surface of an inert silica support is being investigated in order to determine the effects of surface immobilization on the thermolysis pathways for these coal model compounds. The studies are relevant to the thermal chemistry of coal which has a crosslinked network structure. Free radicals formed by thermal bond breaking in coal would remain bonded to the residual macromolecular framework and, hence, be subject to restraints on mobility. We have previously described the procedures for the preparation and thermolysis of these surface immobilized model compounds.²

We have now completed a thorough study of the thermolysis of surface immobilized bibenzyl, $\sim\text{Ph}(\text{CH}_2)_2\text{Ph}$ (1), at various conversions, tem-

peratures, and surface coverages. The results show a dramatic change in product composition from thermolysis of **1** compared to that from liquid or vapor phase bibenzyl. Thermolysis of **1** at 350–400°C at modest conversion levels (0.5–28%) gave as volatile products (in order of generally decreasing molar amounts):

toluene (PhCH₃, **2**), ethylbenzene (PhC₂H₅, **3**), benzene (PhH, **4**), bibenzyl (PhCH₂CH₂Ph, **5**), styrene (PhC₂H₃, **6**), and stilbene (PhCH = CHPh, **7**). The phenolic products, corresponding to the surface attached species in parentheses, were even more numerous: *p*-(1-phenylethyl)-phenol (~~PhCHPhCH₃, **8**), *p*-cresol (~~PhCH₃, **9**), 9,10-dihydro-3-phenanthrenol (~~PhenH₂, **10**), 3-phenanthrenol (~~Phen, **11**), *p*-ethylphenol (~~PhC₂H₅, **12**), phenol (~~PhH, **13**), *p*-(2-phenylethenyl)phenol (~~PhCH = CHPh, **14**), an unidentified isomer of C₁₄H₉OH ("~~Phen isomer," **15**), the two *p*-hydroxylated isomers of 1,2,3-triphenylpropane (~~PhC₃H₅Ph₂, **16**), *p*-benzylphenol (~~PhCH₂Ph, **17**), *p*-(1-phenylethenyl) phenol (~~PhCPh = CH₂, **18**), and dehydrodimers of composition C₂₈H₂₄(OH)₂ (**19**).

Quantitative data for these 18 products formed from thermolysis of **1** with the highest surface coverage used (0.465 mmol g⁻¹ or ~1.4 molecules nm⁻²) were obtained at 400°C (4.2–21.1% conversion), 375°C (0.45–28.4% conversion), and 350°C (0.16–2.4% conversion). Analogous data were obtained at lower coverages consisting of a 4.5-fold variation in coverage at 400°C and a 10-fold variation at 375°C.

A comparison of the thermolysis of **1** with that of fluid bibenzyl revealed a significant acceleration in the overall reaction rate for the surface immobilized case. Furthermore, although there are clear parallels between classes of products in the surfaced attached and fluid states, surface attachment produced major changes in product distributions. For example in the liquid phase at low conversions PhCH₃, dehydrodimers (e.g., (PhCH₂CHPh)₂), PhCH = CHPh, and Ph₂CHCH₃ (56, 21, 10, and 10 mol % respectively) account for the majority of the products.³ However, the analogous products from the thermolysis of **1** at a similar conver-

sion (**2** + **9**, **19**, **7** + **14**, and **8**) are formed in very different amounts (12, 0.6, 4, and 66 mol % respectively). In addition many other products obtained from the thermolysis of **1**, such as the cyclized products **10** and **11**, (summing to about 8 mol %) are not even observed in the low conversion thermolysis of liquid bibenzyl. We have explored the mechanistic factors that underlie the similarities and major differences in the thermal behavior of liquid and surface immobilized bibenzyl, and a few of these features will now be highlighted.

Homolysis. The initial event in the thermolysis of **1** is the homolytic breaking of the weakest bond.

The kinetics of homolysis step (1) were studied at various surface coverages, and first order rate constants at 400, 375, and 350°C of 7.3×10^{-6} , 1.13×10^{-6} , and $0.17 \times 10^{-6} \text{ s}^{-1}$, respectively, were determined. An Arrhenius treatment of these data yields $E_a = 62.7 \text{ kcal/mol}$ and $A = 10^{15.2} \text{ s}^{-1}$, values that correspond closely to those reported for the thermolysis of liquid bibenzyl in tetralin.⁴ Hence it appears that surface attachment has not fundamentally altered the initial C–C homolysis event.

Hydrogen Atom Transfer and Induced Decomposition. The decomposition of additional surface attached bibenzyls is induced by hydrogen atom transfers such as those shown in Eqs. 2 and 3 which form the free and surface attached toluene products. The occurrence of step (3)

indicates that there must be enough conformational mobility of species **1** and $\sim\text{PhCH}_2\cdot$ on the surface to allow the oriented encounter between nearest neighbors needed for hydrogen

atom transfer. We have recently observed that hydrogen transfer steps (2) and, in particular, (3) are hindered by the presence of surface-attached biphenyl ($\sim\text{Ph-Ph}$) groups which act as surface "spacer" units. The inability of many of the C_7 radicals to "find" a nearby $\underline{1}$ for hydrogen transfer apparently results in an unexpected substitution reaction for these radicals on the biphenyl moiety.

The most dramatic change from the fluid phase results is in the different radical decay pathways observed for radical $\underline{20}$. In particular, the coupling of these radicals to form dehydrodimers $\underline{19}$ is markedly reduced (from 21 to 0.6 mol %). This appears to be a direct consequence of surface immobilization which prevents free diffusion of $\underline{20}$. The major reaction pathways observed for radical $\underline{20}$ involve rearrangement and cyclization.

Rearrangement. The dominant product formed from the thermolysis of $\underline{1}$ is the rearranged product $\underline{8}$. The formation of $\underline{8}$ results from a radical chain decay path for $\underline{20}$ as shown in steps (4) and (5).

$\underline{21}$

$\underline{8}$

The minor products $\sim\text{PhCH}_2\text{Ph}$ ($\underline{17}$) and $\sim\text{PhCPh} = \text{CH}_2$ ($\underline{18}$) also appear to derive from the rearrangement process. We can define a kinetic chain length L_R for this path as the ratio of the moles of products formed from the rearrangement ($\underline{8} + \underline{17} + \underline{18}$) to the number of radicals produced in the homolysis step (1) (given by $\underline{2} + \underline{2} + \underline{16}$). At 375°C an examination of the initial reaction behavior (following a very brief inhibition period) yields $L_R = 5.8$, a value that does not vary significantly with temperature over the 350–400°C range studied.

The chain length for rearrangement on the surface is some 30-fold larger than the corresponding L_R for liquid bibenzyl thermolysis. The reason for this increase lies in the

enhanced lifetime of radical $\underline{20}$ arising from surface immobilization, which greatly suppresses the coupling reaction between two of these radicals and hence suppresses the principal termination step for the chain rearrangement sequence (4) and (5). The value of L_R decreases significantly with longer reaction times and with lower surface coverages. In both cases these decreases probably reflect a significant decrease in the rate of step (5) as it becomes more and more difficult for the rearranged surface radical $\underline{20}$ to find a neighboring molecule of $\underline{1}$ at an accessible distance and favorable conformation for transfer of a hydrogen atom.

Cyclization and Unsymmetrical Cleavage. We reported previously that radical $\underline{20}$ also undergoes cyclization first to $\sim\text{Phen H}_2$ ($\underline{10}$) followed by aromatization to $\sim\text{Phen}$ ($\underline{11}$).² If a formal chain length L_C is defined for the formation of $\underline{10} + \underline{11}$ analogously to L_R , we find L_C responds in the same manner as L_R to changes in reaction conditions (temperature, surface coverage, and conversion level including the brief inhibition period). Thus the cyclization path may also have a chain character, with its observed enhancement for surface immobilized $\underline{1}$ compared to liquid bibenzyl again arising from restrictions on the rate of termination reactions for radical $\underline{20}$.

An unsymmetrical cleavage pathway, which produces $\sim\text{PhC}_2\text{H}_5$ ($\underline{12}$) + PhH ($\underline{4}$) and $\sim\text{PhH}$ ($\underline{13}$) + PhC_2H_5 ($\underline{3}$) + PhC_2H_3 ($\underline{6}$), also emerges from obscurity to significance upon surface immobilization of bibenzyl. An examination of the stoichiometric relationships suggests a mechanistic connection between the cyclization and unsymmetrical cleavage processes. A simplified version of our current hypothesis is shown in steps (6–8).

$\underline{10}$

Some of the hydrogen atoms do not cause hydrodealkylation (step 7) but are lost as H_2 (detected qualitatively) according to step (9).

additional unsymmetrical cleavage appears to accompany the dehydrogenation of $\underline{10}$ to $\underline{11}$. These results complement a growing body of new information indicating that strong aryl-alkyl bonds in coal can be cleaved at modest temperatures by internally generated hydrogen atoms without the need for added hydrogen gas.

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2.6.2 Surface Immobilized 1,3-Diphenylpropane

(A. C. Buchanan, III, J. E. Leach,¹
M. L. Poutsma)

Previous studies showed that 1,3-diphenylpropane (DPP), $\text{Ph}(\text{CH}_2)_3\text{Ph}$, cracks at 345-425°C to give, at low conversions, toluene ($\underline{1}$) and styrene ($\underline{2}$).^{2,3} The rate of this reaction was some four orders of magnitude faster than predicted from the strength of the weakest C-C bond in DPP.

Detailed kinetic and isotopic labelling studies revealed that the enhanced rate of reaction resulted from the incursion of an effective

radical chain pathway whose propagation steps are shown in Eqs. 2 and 3.²

We have begun an investigation of the thermolysis of surface attached 1,3-diphenylpropane ($\underline{3}$) to explore the possible perturbations on reactivity arising from surface immobilization. Surface attached $\underline{3}$ was prepared by the condensation of $\text{HOPh}(\text{CH}_2)_3\text{Ph}$ with the surface hydroxyls of a fumed silica by the same methodology used previously to prepare surface attached bibenzyl.⁴ The starting material, $\text{HOPh}(\text{CH}_2)_3\text{Ph}$, was synthesized by the acid catalyzed condensation of cinnamyl alcohol ($\text{PhCH}=\text{CHCH}_2\text{OH}$) and phenol⁵ followed by catalytic hydrogenation of the olefinic intermediate.

A few thermolyses of $\underline{3}$ at 375°C and high surface coverage (0.586 mmol g⁻¹ or 1.7 molecules nm⁻²) have now been performed. Surface attached $\underline{3}$ reacts rapidly at 375°C, and preliminary results from our lowest conversion run (3% conversion after 10 min at 375°C) showed only the five products indicated in Eq. 4.

The small amount of $\underline{6}$ formed appears to result from a secondary reaction of $\underline{4}$ and $\underline{5}$. The product ratio ($\underline{4} + \underline{2}$):($\underline{5} + \underline{1}$) is near unity suggesting that the two distinct benzylic radicals ($\underline{7}$ and $\underline{8}$) are formed with equal probability (like step (2)), and that both undergo

facile β -scission (like step (3)) as shown in Eqs. 5 and 6.

The observed rate of decomposition of 3 ($\sim 21\%$ h^{-1}) is very similar to that reported for liquid DPP ($\sim 20\%$ h^{-1}) at this temperature.² Hence the overall thermal behavior of 3 at low conversion suggests that the radical chain decomposition route found for liquid DPP can still operate under surface immobilized conditions.

At higher conversions we observe that 4 and in particular 5 are increasingly consumed in secondary reactions that require further elucidation. Interestingly we also find an increasing tendency to favor the radical chain pathway that produces 4 and 2 over the pathway

that produces 5 and 1. Future studies may reveal if this phenomenon is a consequence of a stereochemical preference for the formation of surface radical 8 relative to 7 and/or some other feature such as a higher rate of consumption of 7 (compared to 8) in secondary reactions.

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3. AQUEOUS CHEMISTRY AT HIGH TEMPERATURES AND PRESSURES

Studies of chemical equilibria and thermodynamic properties of electrolyte solutions at high temperatures and pressures are the concern of this program. Results help establish bases for fundamental understanding of chemical reactivity and its predictability. Recent emphasis has been given to the application of ion-interaction models to the excess thermodynamic properties of HCl(aq) (3.1.1), alkali metal sulfates (3.1.4) and some salts of carbonic acid and boric acid (3.1.6). Experimental results are reported for calorimetric measurements of the enthalpy of dilution of NaOH(aq) (3.1.2) and isopiestic measurements on mixed electrolytes (3.1.3). A model with three additive contributions to the excess Gibbs energy of mixing has been applied to very concentrated multicomponent electrolytes (3.1.5).

Potentiometric techniques have been applied to the identification of species and measurement of equilibrium quotients in the chromium(VI)(aq) system (3.2.1) and for measurement of the quotients for the dissociation of water in a non-complexing medium (3.2.6). An evaluation of the electrical conductance of water to 1000°C (3.2.2) and a model for the activity of water over electrolyte and non-electrolyte solutions based on a modification of Raoult's Law (3.2.7) are reported. Recent results on the effects of dioxane on two-liquid phase behavior in phosphate systems (3.2.3), spectral and kinetics studies on HOI(aq) (3.2.4), and the description of a new Raman cell for high temperatures and pressures complete the section (3.2.5).

3.1 Thermodynamics of Electrolyte Solutions

3.1.1 Thermodynamics of HCl(aq) to 648 K and

40 MPa

(H. F. Holmes, R. E. Mesmer)

Enthalpies of dilution in the $\text{HCl-H}_2\text{O}$ system have been measured (at ORNL by Busey, Archer, and Mesmer¹) to 648 K and 40 MPa over the molality range of 0.01 to 15.6 $\text{mol}\cdot\text{kg}^{-1}$. These enthalpies are of limited use unless they are combined with other thermodynamic results for the same system, primarily excess Gibbs energies and secondarily, heat capacities, preferably as a function of temperature, pressure, and molality. It is necessary to use some type of model in order to accomplish the combination of thermodynamic properties. The most widely used model for the molality dependence of the excess properties is the ion-interaction model². Application of the simple ion-interaction model is normally limited to ionic strengths of less than 6 to 8 $\text{mol}\cdot\text{kg}^{-1}$ and to systems where ion association is absent or is small enough to be neglected.

In the ion-interaction model the excess Gibbs energy, G^{Ex} , for a 1-1 electrolyte in n_w kilograms of solvent is given by

$$G^{\text{Ex}}/n_w RT = f_G + 2m^2(B + mC), \quad (1)$$

where R is the gas constant, T is the temperature in Kelvins, f_G is the long-range electrostatic (Debye-Hückel) term, m is the molality, and B and C are short-range interaction (repulsive) terms usually referred to as the second and third virial coefficients, respectively. B is dependent on ionic strength and for a 1-1 electrolyte is given by

$$B = \beta^{(0)} + 2\beta^{(1)} [1 - (1 + \alpha m^{1/2}) \exp(-\alpha m^{1/2})]/(\alpha^2 m), \quad (2)$$

where $\beta^{(0)}$ and $\beta^{(1)}$ are interaction parameters and α is a constant usually fixed at 2.0 $\text{kg}^{1/2}\cdot\text{mol}^{-1/2}$. Other thermodynamic functions are obtained from the appropriate derivatives of (1).

The problem reduces to finding a suitable function for the temperature and pressure dependence of $\beta^{(0)}$, $\beta^{(1)}$, and C without an excessive number of adjustable parameters. In the case of HCl(aq) it was found that the number of adjustable parameters necessary to describe the thermodynamics properties could

be greatly reduced if one uses the density of pure water as an independent variable, i.e.,

$$\beta^{(0)} = A_1 + A_2 \ln(\rho^*/\rho_R^*) + A_3(\rho^* - \rho_R^*) + A_4(T - T_R), \quad (3)$$

where the A's are temperature and pressure independent adjustable parameters, ρ^* is the density of pure water and ρ_R^* and T_R are taken as 997.062 kg·m⁻³ and 298.15 K, respectively. Analogous functions are used for $\beta^{(1)}$ and C. The simple ion-interaction model, equation (1), works quite well for HCl(aq) through 523.15 K up to 7 mol·kg⁻¹ and to at least 40 MPa (the high pressure limit of the ORNL results) with only eight adjustable parameters (the A's) to describe the temperature and pressure dependence of $\beta^{(0)}$, $\beta^{(1)}$, and C. The validity of the model can be extended to a molality of 16 mol·kg⁻¹ by adding a term containing a fourth virial coefficient, i.e.,

$$G^{Ex}/n_W RT = f_\phi + 2m^2(B + mC + m^2D) \quad (4)$$

where D is also given by equation (3).

When applied to HCl(aq) above 523.15 K the simple ion-interaction model gives misleading results because of the significant ionic association above 523.15 K. A modification³ of the ion-interaction model can treat associating systems for reasonably small values of the association constant ($K_a < 100$). The modification consists of using an additional interaction parameters, $\beta^{(2)}$, in the second virial coefficient, i.e.,

$$B = (2) + 2\beta^{(2)} [1 - (1 + \alpha_2 m^{1/2}) \exp(-\alpha_2^2 m)] / (\alpha_2^2 m). \quad (5)$$

where the first term refers to equation (2). In fitting the ORNL enthalpy results between 523.15 K and 648.15 K (these are the only thermodynamic data for HCl(aq) in this temperature range) we have taken the temperature and pressure dependence of $\beta^{(2)}$ to be given by

$$\beta^{(2)} = A_1(T - T_R) \ln(\rho^*/\rho_R^*) + A_2(T - T_R)(\rho^* - \rho_R^*), \quad (6)$$

where ρ_R^* and T_R are taken as 997.062 kg·m⁻³ and 298.15 K, respectively, for this temperature range. With this modification we are able to fit the high temperature (523.15 to 648.15 K) ORNL enthalpy results with a standard error of fit of about eight percent. One would like a better fit but the deviations are random and there is reasonable agreement with results from a much more complex model which explicitly considers ionic association⁴.

Since they are of the same charge type it is interesting to compare the recently published activity coefficients of NaCl(aq)⁵ with those for HCl(aq) obtained from the present work. This is done in Fig. 3.1, which shows the logarithm of the activity coefficient as a function of $m^{1/2}$ between 298.15 and 573.15 K. The prominent trend with temperature in Fig. 3.1 is that both activity coefficients decrease with increasing temperature. However, the activity coefficient of HCl(aq) decreases much faster with the two activity coefficients becoming about equal at 523.15 K (they differ by no more than five per cent at this temperature) while at 573.15 K γ for HCl(aq) is about 30 per cent less than γ for NaCl(aq) at high molalities. A simple descriptive explanation is that $H^+(aq)$ is hydrated more strongly than $Na^+(aq)$ at low temperatures, resulting in a larger γ for HCl(aq). With increasing temperature the dielectric constant and hydration energy both decrease causing γ for both salts to decrease, albeit at a faster rate for HCl(aq). Above 523.15 K ion association becomes greater for HCl(aq) than for NaCl(aq), resulting in a lower γ for HCl(aq).

We now have equations for all of the excess thermodynamic properties of HCl(aq) from 273.15 to 648.15 K, from 0 to 16 mol·kg⁻¹, and to at least 40 MPa.

Fig. 3.1. Logarithm of the activity coefficients of NaCl(aq) and HCl(aq) as a function of the square root of the molality at saturation pressures. Points are for identification only.

3.1.2 The Enthalpy of Dilution of NaOH(aq) to 673 K and 40 MPa

(J. M. Simonson, R. E. Mesmer)

The heat and liquid flow microcalorimeter developed in this program¹ has been used to measure enthalpies of dilution of a strong acid² and chloride salts^{1,3} at temperatures to 673 K. There is intrinsic interest in the thermodynamics of an aqueous strong base under corresponding conditions. Dilution enthalpy data for aqueous sodium hydroxide have been obtained over the ranges $298 < T/K < 673$, $70 < P/\text{bar} < 400$ and $0.008 < m/(\text{mol}\cdot\text{kg}^{-1}) < 6.3$. These data are required to analyze the results of anticipated studies of weak acid neutralization reactions at high temperatures and pressures. In addition, excess thermodynamic properties as functions of temperature, pressure and composition may be calculated from this new experimental information.

Care was taken throughout this study to minimize contamination of the base solutions by atmospheric CO_2 . A 50 wt % NaOH aqueous solution was allowed to stand until the small amount of solid carbonate present had settled out. Stock solutions of 6.3, 1.0, 0.2 and $0.05 \text{ mol}\cdot\text{kg}^{-1}$ NaOH were prepared by diluting the 50 wt % solution with CO_2 -free deionized water. All solution handling was done under an argon atmosphere. Solutions were standardized by potentiometric titration with standard HCl solution. Analysis of the neutralization curves indicated that carbonate contamination was less than 0.1 mol % in all stock solutions.

Deionized water used in the calorimetric dilutions was thoroughly sparged with argon. A range of dilution ratios was used to obtain smooth dilution curves with a minimum number of stock solutions. Replicate measurements were consistent within 1% for the runs at higher concentrations ($> 1 \text{ mol}\cdot\text{kg}^{-1}$); precision at lower concentrations was within 4%. These results are comparable to those obtained previously¹⁻³.

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Dilution enthalpies referenced to the 6.3 molal stock solution are plotted in Figs. 3.2 and 3.3. Values of the pressure coefficient of the enthalpy of dilution at high temperatures are shown in Fig. 3.4. A remarkable result at low temperature (298 K) is the presence of a minimum in the dilution enthalpy curve. While the results obtained previously for HCl(aq)^2 and $\text{CaCl}_2(\text{aq})^3$ show a region of relatively small change of apparent relative enthalpy with concentration, these systems do not have the clear minimum of the NaOH curve. It is also of interest to note that the dilution enthalpy curve at 323 K has no minimum in this concentration region, indicating a strong temperature dependence of the dilution enthalpy at modest concentrations.

Ion pairing has been suggested as an explanation of the "anomalous" behavior of the alkali metal hydroxide activity coefficients

Fig. 3.2. Enthalpy of dilution of NaOH(aq) at 7.0 MPa relative to a 6.3 mol·kg⁻¹ stock solution plotted against the square root of the diluted solution molality.

Fig. 3.3. Enthalpy of dilution of NaOH(aq) at high temperatures relative to a 6.3 mol·kg⁻¹ stock solution plotted against the square root of the diluted solution molality.

at low temperatures as compared with the corresponding chloride salts⁴. However, the dilution enthalpies at low temperatures do not exhibit the behavior taken to characterize ion association at higher temperatures³. Based on this observation, it seems unlikely that ion association is responsible for the observed differences in alkali chloride and hydroxide excess thermodynamic properties at low temperatures.

Dilution behavior characteristic of associating electrolytes has been observed at temperatures above 573 K in all systems studied to date¹⁻³. Comparisons of the low concentration regions of the dilution curves of NaCl(aq) , HCl(aq) and NaOH(aq) indicate that the hydroxide system is likely less strongly associated than HCl(aq) , and quite similar to NaCl(aq) . Quantitative modeling of the calorimetric results with the ion association-interaction model⁵ will be

Fig. 3.4. Pressure coefficient of the enthalpy of dilution of NaOH(aq) at high temperatures relative to a 6.3 mol·kg⁻¹ stock solution plotted against the square root of the diluted solution molality.

carried out in the near future, when the necessary association constant values for NaOH(aq) will be available from conductance studies.

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3.1.3 The CsCl - BaCl₂ - H₂O Mixed Electrolyte System at Elevated Temperature

(H. F. Holmes, R. E. Mesmer)

Thermodynamic properties of mixed electrolytes are normally described by an

appropriate summation of the properties of the pure components plus functions of one or more mixing parameters. Most investigators, including ourselves, use the ion-interaction model¹ for this purpose. As an example, the osmotic coefficient, ϕ , of a mixture of two 1-1 electrolytes, MX and NX, having a common anion, X, is given as

$$\phi = (1-y) \phi_{MX}^* + y \phi_{NX}^* + y(1-y)m(\theta_{MX} + \theta_{NX}) \quad (1)$$

where ϕ^* is the osmotic coefficient of the pure component (MX or NX) at the same total molality, m , as the mixture, and y is the mole fraction of NX. θ_{MX} and θ_{NX} are binary and ternary mixing parameters, respectively, whose values are determined from a fit of eq. (1) to experimental results.

It is desirable to search for systematics, contributing factors, and the importance of θ and ϕ in eq. (1) in order to make estimates and predictions. Our previous studies of mixed electrolytes systems at high temperatures have been limited to common ion systems involving NaCl and another alkali or an alkaline earth metal chloride⁽²⁻⁴⁾. These studies showed that the temperature dependence of the binary mixing parameter, θ_{NaM} , varied systematically with the ion size of M for mixtures of NaCl and MCl where M is an alkali metal other than Na. Cesium and barium are the largest and least hydrated of the alkali and alkaline earth metals, respectively, and, at 298.15 K, have the largest binary mixing parameter of any two cations listed in Pitzer and Kim⁵.

These factors led us to undertake an isopiestic study of [(1-y) CsCl + yBaCl₂] (aq) over the temperature range of 383.15 to 523.15 K using NaCl(aq) as the reference electrolyte. Analysis of the results have not been completed at the present time, but the data at 473.15 K will serve as an informative example of the information we have obtained for this mixed electrolyte system.

The importance of mixing parameters in the Cs + Ba system is demonstrated by the fact that the osmotic coefficients of the mixture can only be predicted to within 3.2 percent if the mixing parameters are taken as zero. This result can be contrasted with the Na + Ca system where the osmotic coefficients could be predicted to 0.5 percent without any mixing parameters³. With mixing parameters, the osmotic coefficients in the Cs + Ba system could be fit to 0.4 per cent. However, it was necessary to use both θ and ϕ to obtain a satisfactory fit and this is the first example where a ternary mixing parameter has been required at elevated temperatures. The results have been analyzed in sufficient detail to know that absolute values of both θ and ϕ are decreasing with increasing temperature, i.e., the mixing parameters are becoming less important at the higher temperatures.

Having the mixing parameters, it is a relatively easy matter to calculate the activity coefficients for $[(1-y) \text{CsCl} + y\text{BaCl}_2] \text{ (aq)}$. These are shown in Fig. 3.5 as a function of molality and ionic strength fraction, x , of BaCl_2 for both components at 473.15 K. The activity coefficient of BaCl_2 is not very dependent on solution composition, varying by not more than about six percent over the entire range from pure CsCl to pure BaCl_2 . In the case of CsCl the activity coefficient is more dependent on composition but only at the higher ionic strengths. Once again this is in contrast to the Na + Ca system where γ was highly dependent on solution composition³. In Fig. 3.5 γ^0 refers to the activity coefficient of a pure component while γ^∞ is the trace activity coefficient, i.e., the activity coefficient of an infinitely dilute component in a pure solution of the second component. Dashed lines in Fig. 3.5 show the importance of mixing parameters for trace components, e.g., the trace activity coefficient of BaCl_2 computed without mixing parameters, can be in error by more than 30 percent. This also illustrates

Fig. 3.5. Logarithm of the activity coefficients of CsCl and BaCl_2 in $[(1-y)\text{CsCl} + y\text{BaCl}_2] \text{ (aq)}$ as a function of the ionic strength, I , and ionic strength fraction, x , of BaCl_2 , at 473.15 K. Superscripts 0 and ∞ indicate pure and trace components, respectively.

the important role of mixing in many geochemical systems.

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3.1.4 Thermodynamics of Aqueous Solutions of the Alkali Metal Sulfates¹

(H. F. Holmes, R. E. Mesmer)

The available thermodynamic data for aqueous solutions of the sulfates of lithium, sodium, potassium, and cesium have been analyzed and correlated to produce a comprehensive mathematical model for the excess thermodynamic properties of these electrolyte solutions. Experimental excess Gibbs energies of the solutions at high temperatures consist entirely of isopiestic results obtained at ORNL², with the ORNL results being the only experimental thermodynamic data for Li_2SO_4 (aq) and Cs_2SO_4 (aq) above 25°C.

Basic equations for the thermodynamic properties of these solutions were taken from the ion-interaction model. As an expedient, the temperature dependence of the ion-interaction parameters was taken to be the same as that used by Rogers and Pitzer³ in treating their high temperature (to 473 K) heat capacity results for Na_2SO_4 (aq).

The success of the ion-interaction model in treating thermodynamic results for aqueous electrolytes is partly due to the fact that the second virial coefficient is dependent on the ionic strength, I . As an example, the second virial coefficient for the osmotic coefficient, B^ϕ , is given by

$$B^\phi = \beta^{(0)} + \beta^{(1)} \exp(-\alpha I^{1/2}), \quad (1)$$

where $\beta^{(0)}$ and $\beta^{(1)}$ are interaction parameters and α is treated as a constant. Pitzer⁴ adopted $2.0 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$ as the value of α to be used for all electrolytes in which at least one ion is univalent. A universal value of α for all electrolytes is, of course, quite convenient but, as Pitzer indicated⁴ α can be adjusted for each electrolyte without loss of the basic features of the ion-interaction model. In the isothermal treatment² of our isopiestic results for the alkali metal sulfates a much superior fit was obtained by setting α at $1.4 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$. The value used

for α was more important at elevated temperature and became more critical on going from lithium to cesium. This value ($1.4 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$) was adopted in our comprehensive model.

With a very few exceptions, our model reproduces the available thermodynamic results for aqueous solutions of the alkali metal sulfates to within their experimental uncertainty. The model is also used for calculating contributions to the excess properties of electrolyte mixtures containing alkali metal sulfates.

Figure 3.6 compares the activity coefficients of the alkaline earth metal chlorides (MCl_2) and those of the alkali metal sulfates (M_2SO_4) at 110 and 200°C. Since the long-range electrostatic contribution (the Debye-Hückel part shown as the limiting law (L.L.) in Fig. 3.6) is the same for both families, this is an especially interesting comparison. The obvious differences are that the activity coefficients of M_2SO_4 are smaller and show much less intrafamily variability. These differences can be related to hydration behavior as evidenced by molar volumes at infinite dilution $\bar{V}_2^\circ$, which, for electrolytes at high temperature, strongly reflect hydration since the large negative volumes observed can only be explained in terms of constriction of the solvent. Also, the intrinsic volume of the unhydrated ions can be eliminated when a difference in molar volumes is considered. Figure 3.7 is plot of the short-range contributions to $\ln \gamma$ ($\ln \gamma$ minus f^Y , the long-range interaction term) against $[\bar{V}_2^\circ(200^\circ\text{C}) - \bar{V}_2^\circ(25^\circ\text{C})]$ as a measure of hydration effects. The monotonic curves show that the position of the $\ln \gamma$ values for the M_2SO_4 (aq) electrolytes is consistent with a smooth trend toward higher values for more strongly hydrated electrolytes. Figure 3.7 does not rule out a contribution due to ionic association (in this case, incomplete dissociation of the MSO_4^- ion), particularly at the higher temperatures, where it is probable

Fig. 3.6. Activity coefficients of H_2SO_4 (aq) and MCl_2 (aq) electrolytes as a function of molality at 110 and 200°C.

Fig. 3.7. Activity coefficients of H_2SO_4 and MCl_2 (aq) electrolytes against molar volumes at infinite dilution: the ordinate in $\ln \gamma - f \gamma$, i.e., the sum of the short-range interaction terms. o, 1.0 mol·kg⁻¹; •, 2.0 mol·kg⁻¹.

that the short-range contribution to $\ln \gamma$ for H_2SO_4 is a combination of hydration and association.

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3.1.5 Thermodynamics of Very Concentrated, Multicomponent Electrolyte Solutions¹

(J. M. Simonson, K. S. Pitzer²)

Many electrolytes show a marked increase in solubility in water with increasing temperature. Mixed-salt systems which melt congruently at moderate temperatures (360 - 523 K) and are completely miscible with water from dilute aqueous solutions to the fused salt are extreme examples of this behavior. Experimental and theoretical investigation of the thermodynamics of prototype systems may be expected to lend insight into the behavior of a broad class of highly soluble electrolytes.

In our experimental investigations, the vapor pressure of water was measured as a function of temperature and solution composition in the system $\text{LiNO}_3\text{-KNO}_3\text{-H}_2\text{O}$. The apparatus used was designed to permit direct measurement of solvent vapor pressures to 450 K³. Degassed samples were maintained at the desired temperature in an air oven thermostat. Pressures were measured with an MKS Instruments Baratron capacitance manometer which was independently thermostated at approximately 10 K above the temperature of the sample. Error in the vapor pressure measurements was estimated from the internal consistency of the calculated water activities to range from 0.5% at the lower temperatures (373-393 K) to 2% at the high temperature

limit (436 K). Experimentally determined water activities are shown as discrete symbols in Fig. 3.8.

A novel approach to modeling must be used to represent the thermodynamic properties of completely miscible electrolyte solutions. The molality becomes infinite for a fused salt; hence, we use the ionized solute mole fraction as the composition scale. It is assumed that the free energy of mixing may be represented as the additive contributions of three terms: an ideal mixing term, a limiting law term which accounts for the electrostatic effects of the solute in very dilute solution, and a nonelectrostatic contribution which may be written as a weighted sum of terms representing specific short-range interactions among solution species. The usefulness of this assumption has been demonstrated in the work of Pitzer^(4,5), where miscible mixtures were treated as pseudobinary solutions to avoid the complications introduced by explicit consideration of multicomponent systems. The generalized multicomponent equations are quite general,

Figure 3.8. Water activity at 393 K for KNO_3 (top curve), $\text{LiNO}_3\text{-KNO}_3$ (50 cation pct. Li , center), LiNO_3 (bottom) solutions. $\circ$, Δ , this study; $\circ$, $\square$, ref. 6; $\blacksquare$, ref. 8. Solid curves calculated from eq. (1).

but are too cumbersome to be of practical use. Combinations of short-range interaction parameters are determinable from measurements on particular classes of systems. For a system with one neutral (solvent) component and two electrolyte solutes having a common ion (MX and NX), the activity of the solvent is given by

$$\begin{aligned} \ln a_1 = & \ln x_1 + 2A_x I_x^{3/2} / (1 + \rho I_x^{1/2}) \\ & + x_I^2 \{ F W_{1,MX} + (1-F) W_{1,NX} \\ & - F(1-F) W_{MX,NX} / 2 + (x_I - x_1) [F U_{1,MX} + \\ & (1-F) U_{1,NX} + F(1-F) Q_{1,MX,NX}] \\ & + x_I F(1-F)(1-2F) U_{M,N} \} \end{aligned} \quad (1)$$

where $x_I = n_I / (\sum n_j)$, $F = n_{Li} / (n_{Li} + n_K)$,

$I_x = 1/2 \sum x_j z_j^2 = 1/2 x_I$ and the subscripts are

$1 = H_2O$, $M = Li^+$, $N = K^+$, $X = NO_3^-$.

Here the adjustable parameters (W's, U's and Q) are observable combinations of parameters in the more fundamental representation, A_x is the Debye-Hückel slope on an ionized mole fraction basis and ρ is a hard-core repulsion parameter which is given a particular value for broad classes of electrolytes. It should be noted that all adjustable parameters of eq. (1) except Q may be determined from thermodynamic measurements on binary solutions. Thus for systems in which the effects of the three-component parameter Q are relatively small, the thermodynamic properties of ternary systems may be estimated from measured properties of binary solutions.

The applicability of eq. (1) to miscible systems has been tested by fitting the thermodynamic data for $LiNO_3$ - KNO_3 - H_2O solutions. Water activity data are available for the $LiNO_3$ - H_2O binary system from the isopiestic results of Braunstein and Braunstein⁶, and for the KNO_3 - H_2O solutions from this study.

Binary parameters for the mixed fused salt $LiNO_3$ - KNO_3 may be determined from phase diagrams⁽⁷⁾; given the limited precision of the available results for this system, we have set $U_{M,N} = 0$ and have determined both $W_{MX,NX}$ and $Q_{1,MX,NX}$ from measurements on the three-component system. Our value for the $W_{MX,NX}$ parameter at 436 K agrees with that calculated from phase studies within the uncertainty of the latter results. Activities of water at 393 K calculated from eq. (1) are shown as solid curves in Fig. 3.8. Agreement between calculated and measured values is excellent at all conditions studied. Other thermodynamic properties of these solutions, including solute activity coefficients and excess enthalpies, may be calculated from the generalized multicomponent model. Analysis of available experimental results for other concentrated multicomponent systems is in progress.

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3.1.6 Excess Thermodynamic Properties of the Salts of Some Weak Inorganic Acids at Temperatures to 368 K

(J. M. Simonson, R. M. Roy¹)

Ionization constants have been determined at ORNL for a number of weak inorganic acids

as functions of temperature, pressure and electrolyte media². Such studies yield information on the identity and relative abundance of species present in solution. Calculation of thermodynamic properties at higher buffer concentrations or in other media requires that the activity coefficients of the various species be known. Thus, it is of interest to study the thermodynamics of these more concentrated systems. Measurements of electromotive force (EMF) are an important source of experimental information on buffer systems. Cells of the type

where HB is a weak acid and MB is the salt of that acid, are particularly useful in determining excess thermodynamic properties at modest temperatures. Here we outline our use of these cells in determining the excess thermodynamic properties of solutions containing carbonate and borate.

I. $\text{H}_2\text{CO}_3 - \text{KHCO}_3$

The experimental methods and data analysis techniques appropriate for this system have been worked out in detail in studies at 278-318 K³. In more recent experimental work, the temperature range has been extended to 368 K. This new information has been used to revise expressions for the temperature dependence of the parameters of Pitzer's ion interaction treatment⁴ pertaining to the carbonate and bicarbonate ions. It was found that a simple linear dependence of the parameters on temperature used in the earlier study was not adequate to represent the higher temperature results. With these new findings, it will be possible to estimate the uncertainty involved in extrapolation of the results for other systems.

II. $\text{B}(\text{OH})_3 - \text{KB}(\text{OH})_4$

This system is of particular interest because the formation of polyborate anions in

solution makes it impossible to study excess properties of this system by other methods. By maintaining a low total concentration of boron in solution (0.04 molal), we have been able to minimize the interference of polyborate formation on the measured thermodynamic properties. The temperature range covered in this study (278-318 K) makes these results particularly applicable to detailed studies of seawater and low temperature natural waters.

III. $\text{B}(\text{OH})_3 - \text{MgB}(\text{OH})_4)_2$ and $\text{B}(\text{OH})_3 - \text{CaB}(\text{OH})_4)_2$

An important result of this study is the discovery that ion pairing effects (e.g., formation of $\text{MgB}(\text{OH})_4^+$) are important in modeling the observed properties. The wide range of ionic strength studied in this work makes it possible to estimate the low values of the ion pairing constant for these systems. This marks the first time that the β_{MX}^2 (approximate ion association) extension of Pitzer's treatment has been shown to be necessary to represent results for 2-1 electrolytes at low temperatures. As noted for the corresponding potassium system, the temperature range of this study will lead to direct application in low temperature and natural water systems.

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3.2 Equilibrium, Kinetics and Speciation

3.2.1 Hydrolysis of Chromium(VI) in NaCl Media to 175°C

(D. A. Palmer, D. Wesolowski, R. E. Mesmer)

The hydrolysis of chromium(VI) was studied in a concentration cell with hydrogen electrodes from 25 to 175°C at 25° intervals and at NaCl molalities of 0.114, 0.235, 0.534, 0.999, 2.940, and 5.239. These results can be interpreted exclusively in terms of the following equilibria:

Selected literature values for the logarithm of the equilibrium quotients, $\log Q_1$, for reaction (1) were combined with the present values, then converted to the basic form - see reaction (1b) - and subjected to a least-squares fit involving four adjustable parameters, as well as a Debye-Hückel term (equation 4),

$$\log Q_{1b} = \log(Q_1/Q_w) = -2S\sqrt{I}/(1+\sqrt{I}) + 0.0157If(I,T) + A/T + B + CI + DIT^2 \quad (4)$$

where Q_w is the equilibrium quotient for the dissociation of water in NaCl solution, S is the Debye-Hückel coefficient, I is the ionic strength, $f(I,T)$ is a function of ionic strength and temperature, and A - D are the adjustable parameters. A plot $\log Q_{1b}$ versus $\sqrt{I}/(1+\sqrt{I})$ is shown in Fig. 3.9 where the curves result from equation (4). This treatment yielded the following molal thermodynamic quantities at infinite dilution and 25°C: $\log K_1 = 6.55(0.04)$, $\Delta H_1 = 5.8(1.0)$ kJ mol⁻¹, $\Delta S_1 = 143(3)$ J K⁻¹ mol⁻¹, $\Delta C_{p,1} = 231(6)$ J K⁻¹ mol⁻¹, and $\log K_{1b} = -7.44(0.03)$.

Fig. 3.9. A plot of $\log Q_{1b}$ vs. $\sqrt{I}/(1 + \sqrt{I})$ for temperatures from 25 to 175°, where $\circ$ represent the values determined in this study while symbols $\square$ and ∇ were calculated from literature data.

The value for ΔH_1 is in good agreement with a literature value determined by calorimetry¹, viz. 2.9 kJ mol⁻¹. Note that by using the basic, or anionic, form of the hydrolysis reaction only anions are involved and hence the change in heat capacity (small at $I = 0.0$), is minimal.

In a similar manner, the best fit of $\log K_{2b}$ for the basic form of reaction (2) was obtained with equation (4) and these results are presented in Fig. 3.10. This treatment gave the corresponding quantities at 25°C: $\log K_2 = 14.68(0.10)$, $\Delta H_2 = -4(2)$ kJ mol⁻¹, $\Delta S_2 = 269(8)$ J K⁻¹ mol⁻¹, $\Delta C_{p,2} = 463(13)$ J K⁻¹ mol⁻¹, and $\log K_{2b} = 13.30(0.08)$. The corresponding calorimetric value for ΔH_2 is -13.9 kJ mol⁻¹.

though inclusion of CrO_3Cl^- rather than the $\text{Cr}_2\text{O}_7\text{H}^-$ species in the overall fit gave significantly better standard deviations, this does not constitute definitive proof for the presence of the former. However, it is significant that reliable formation quotients could only be assigned at the higher chloride concentrations (i.e., > 1m) and then generally at the higher temperatures. The latter factor appears to originate from slow kinetics in the pH range 4-2 where this spe-

Fig. 3.10. A plot of $\log Q_{2b}$ vs. $\sqrt{I}/(1 + \sqrt{I})$ for temperatures for 25 to 175°C, where the symbols are as defined in Fig. 3.9.

cies was significant. The $\log Q_{3b}$ values (see Fig. 3.11) associated with the basic form of this reaction were fitted by two different methods, the preferred of which (represented by the dashed lines in Fig. 3.11) resulted in the following: $\log K_3 = 7.49(.21)$, $\Delta H_3 = 11(2) \text{ kJ mol}^{-1}$, $\Delta S_3 = 181(6) \text{ J K}^{-1} \text{ mol}^{-1}$, $\Delta C_{p,3} = 610(13) \text{ J K}^{-1} \text{ mol}^{-1}$, and $\log K_{3b} = -20.50(0.19)$ at 25°C. In 1M sodium perchlorate solution a $\log Q_3$ value of 6.80 was reported², which is in reasonable with the value obtained in 1M NaCl solution of 6.63(.19) at 25°C.

Fig. 3.11. A plot of $\log Q_{3b}$ vs. $\sqrt{I}/(1 + \sqrt{I})$ for temperatures from 75 to 175°C.

Practical applications of aqueous chromate(VI) chemistry are found in the anodic treatment of aluminum and the froth flotation processing of galena. Moreover, chromate(VI) is toxic to the environment and is apparently the dominant form of mobile chromium in non-reducing surface waters. Finally, a knowledge of the thermodynamics of these equilibria coupled with a spectrophotometric analysis of the same solutions, may allow this system to serve as a pH indicator in other oxidizing, high temperature systems where use of hydrogen electrodes may not be possible.

¹L. G. Hepler, J. Am. Chem. Soc. 80, 6181 (1958).

²Calculated from the original reference, J. Y. Tong and R. L. Johnson, Inorg. Chem., 5, 1902 (1966), and the $\log Q_1$ value of 5.755(.004) in 1M NaCl (this work).

3.2.2 Evaluation of the Electrical Conductance of Water, 0-1000°C and up to 1000 MPa¹

(W. L. Marshall)

Reliable values of the electrical conductance of pure water at high temperatures are useful as background conditions for estimating ionic impurities by conductance measurements in steam cycles as well as for their fundamental value. However, because of difficulties in obtaining and maintaining absolutely pure water, there are only a few experimental measurements on the electrical conductance of water substance at high temperatures.

The best procedure to obtain the needed conductances of water is by an indirect method that applies (1) the extent of ionization of water as expressed by its ion product (K_w) and (2) the molar conductance, which is equal to the sum of the limiting ionic conductances of the hydrogen ion [$\lambda_o(H^+)$] and the hydroxide ion [$\lambda_o(OH^-)$]. An equation providing calculated values of K_w as a function of temperature from 0 to 1000°C and pressures up to

1000 MPa is available elsewhere as an International Association for the Properties of Steam (IAPS) standard².

Previously in this activity, correlations of $\lambda_0(\text{H}^+)$ and of $\lambda_0(\text{OH}^-)$ as a function of density and temperature were developed that could be combined with K_w and density to establish an equation for calculating specific electrical conductances of water to extremes of temperature and pressure³. In this present study, a simplicity in the behavior of the limiting electrolyte conductances has been discovered in that several isothermal plots of $\Lambda_0(\text{electrolyte})$ versus density appear to extrapolate to a common value of density at which the conductance becomes zero. This condition is hypothetical since it is at much too high a density to be obtained experimentally. Also, at low temperatures water would solidify before it could be reached. A description of the behavior for aqueous NaCl is shown in Fig. 3.12. With adherence to this behavior, the fractional decrease in $\Lambda_0(\text{NaCl})$ per unit increase in density is the same at any given temperature. The many electrolytes studied in this activity over the past several years are discovered to behave similarly.

Fig. 3.12. The Limiting Equivalent Conductances of Aqueous Sodium Chloride Solutions versus Density, 0 - 800°C.

The values of $\Lambda_0(\text{H}^+, \text{OH}^-)$ at a given temperature and pressure, calculated from results of previous studies⁴⁻⁶,

$$\Lambda_0(\text{H}^+, \text{OH}^-) = \Lambda_0(\text{HCl}) + \Lambda_0(\text{NaOH}) - \quad (1)$$

$$\Lambda_0(\text{NaCl}),$$

agree with those evaluated from the sum of the values of $\lambda_0(\text{H}^+)$ and $\lambda_0(\text{OH}^-)$ obtained independently at saturated vapor pressures⁷.

By using the observed relationships, the following is obtained for water,

$$\kappa_w = \Lambda_0(\text{H}^+, \text{OH}^-) \cdot \sqrt{K_w} \cdot (0.001) \cdot \rho_w \quad (2)$$

where

$$\Lambda_0(\text{H}^+, \text{OH}^-) = [\rho_w - 14.12] \cdot S \quad (3)$$

and

$$S = S_{HT} - 1/[1/(S_{HT} - S_0) - A_1 \cdot t - A_2 \cdot t^2 - A_3 \cdot t^3] \quad (4)$$

where

$$A_1 = +7.58199 \times 10^{-5}$$

$$A_2 = -4.64165 \times 10^{-7}$$

$$A_3 = +7.93347 \times 10^{-9}$$

$$S_{HT} = -131.$$

$$S_0 = -25.15$$

In Eqs (2)-(4), ρ_w is the density (g cm^{-3}) of water, S is the isothermal slope of $\Lambda_0(\text{H}^+, \text{OH}^-)$ versus density at a given temperature, S_{HT} and S_0 are the evaluated slopes at 400-1000° and 0°C, respectively, t is temperature in °C, and k_w is the specific conductance in siemens cm^{-1} ($\text{ohm}^{-1} \text{ cm}^{-1}$).

This new conductance equation is believed to describe the specific conductance of

liquid water within ± 1 to $\pm 3\%$ at temperatures up to 374°C and at pressures up to 1000 MPa. For supercritical water fluid at pressures from 30 to 1000 MPa and at temperatures from 374°C to 1000°C , the uncertainties probably will increase from 3% at the low temperatures and pressures to perhaps 15% at the highest temperatures and pressures.

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3.2.3 Two-Liquid-Phase Formation at High Temperatures for Na_2HPO_4 Dissolved in Dioxane-Water Solutions.

(W. L. Marshall)

Disodium hydrogen phosphates in the past have been added to steam generator cycles as buffering agents for corrosion inhibition. Difficulties have arisen, however, in that sometimes corrosion has been enhanced rather than hindered. This behavior may be attributed to several factors, one of which possibly is the formation of an immiscible concentrated liquid phase at the usual temperatures of operation (275 – 325°C) of steam power cycles^{1,2}. Previously in this activity we discovered that dipotassium hydrogen phosphates also produced second liquid phases, but their temperatures of formation (360 – 380°C) were much above the usual

operating temperatures. We, therefore, proposed that potassium salts be substituted for sodium salts and that investigations be made to determine whether these salts would alleviate the problems observed for the sodium salts^{1,2}. The present study is an outgrowth from this work to explore the behavior of an added solvent, dioxane, in changing the temperatures of formation of the second liquid phases. Dioxane is completely miscible with water, has a dielectric constant close to 1 (and thus is essentially non-polar), and is seemingly stable at temperatures up to the critical temperature of water (374°C)³. It was therefore of much interest to observe its effect on temperatures of liquid-liquid immiscibility and to try to explore a fundamental relationship between dielectric constant of the solvent and liquid-liquid immiscibility.

Solutions containing several compositions of Na_2HPO_4 dissolved in various solvent mixtures of dioxane and water were prepared. These solutions were sealed in fused silica capillary tubes in the same manner as described previously^{2,3}, and they were heated to temperatures of 200 to 400°C in obtaining the temperatures of formation of concentrated second liquid phases. Some of the results are plotted in Fig. 3.13 as temperature of immiscibility versus the weight percent Na_2HPO_4 in water and in two compositions of dioxane-water. It is evident that added dioxane drastically lowers the immiscibility temperature for a given composition of Na_2HPO_4 . From other studies⁴, we have estimated several needed physical properties of these dioxane-water solvents including dielectric constant and density. With these properties, we are exploring relationships that might provide some simple correlations either with density of contained water or dielectric constant. As seen in Fig. 3.13 a lowered dielectric constant (resulting from the added dioxane) or lowered solution density of water lowers the immiscibility temperature as might be expected.

Fig. 3.13. Effect of Added Dioxane Solvent on Temperatures of Immiscibility for $\text{Na}_2\text{HPO}_4\text{-H}_2\text{O}$ Solutions (** Wt.% Dioxane based on salt weight + total solvent weight).

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3.2.4 Spectral Characterization and Kinetics of Formation of Hypiodous Acid

(D. A. Palmer, R. van Eldik¹)

The kinetics of disproportionation of the halogens in aqueous solution as represented by eq 1 were studied by Eigen and Kustin² using the then relatively new technique of temperature-jump spectrophotometry.

They established a common rate law for the three halogens, $\text{X} = \text{Cl}, \text{Br}$ and I , viz.,

$$k_{\text{obs}} = k_1 + k_{-1} \frac{[\text{HOX}][\text{H}^+]}{[\text{HOX}][\text{I}^-] + [\text{H}^+][\text{I}^-]} \quad (2)$$

with $k_1 = 3 \text{ s}^{-1}$ and $k_{-1} = 4.4 \times 10^{12} \text{ m}^{-2} \text{ s}^{-1}$ for $\text{X} = \text{I}$ at 20°C and at an ionic strength of 0.1M (KNO_3). However, a reinvestigation of the iodine reaction at the same experimental conditions gave rates incompatible with the third-order term; despite the fact that the new results were obtained over a much wider pH range, 2.95 to 7.06, compared to 4.0 to 5.0², k_{obs} was found to be independent of the proton concentration. These new results are presented in Table 3.1.

Table 3.1. Summary of Kinetic Data Pertinent to Iodine Disproportionation

pH	$10^4[\text{I}_2]$	$10^5[\text{I}^-]$	$10^6[\text{HOI}]$	k_{obs}^a
	M	M	M	s^{-1}
2.95	6.82	3.50	0.0115	1020±50
3.62	8.42	2.89	0.0759	970±50
4.44	8.37	3.00	0.480	980±20
5.27	8.96	3.19	3.28	970±40
5.35	8.95	3.04	4.13	950±70
5.36	8.71	2.93	4.25	980±40
5.75	8.74	3.20	9.59	1040±40
7.06	4.99	8.92	40.2	1050±40

^aEach k_{obs} value represents the mean of eight measurements.

As in the previous study, the iodine disproportionation reaction was monitored indirectly by observing the spectral changes associated with I_3^- formation according to eq 3.

The triiodide ion has a very strong absorption maximum at 350nm (absorptivity of 25800

$\text{M}^{-1} \text{cm}^{-1}$) which serves as a very sensitive indicator for small changes in the iodide concentration resulting from the temperature perturbation of eq 1. In addition, reaction 3 is known³ to be considerably faster than reaction 1. The reaction sequence consistent with these results involves the intermediate I_2OH^- ion.

Furthermore, the k_{obs} values in Table 3.1 must be assigned almost entirely to the forward k_3 path, thus giving a mean value for this first-order rate constant of $994 \pm 36 \text{ s}^{-1}$ at 20°C . From the value⁴ of the corresponding equilibrium constant, K_3 ($=k_3/k_{-3}$), of 3.1×10^{-3} , a k_{-3} value of $3.2 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ can be calculated. Hence, even at the highest concentrations of HOI and I^- studied the k_{-3} term only contributes 4% to the overall value of k_{obs} . Physical and chemical restraints on this system do not allow either concentration to be raised significantly beyond the maximum values described here so that it is unlikely that the k_{-3} step will ever be observed without recourse to a stopped-flow, temperature-jump method. Even then as the pH of the solution is raised reaction 6 becomes increasingly important with the expected result that the

rate of formation of I_2OH^- would eventually exceed the rate of disproportionation (eq. 5) and the rate law would revert to the general form shown in eq 2. Estimates for the values of k_2 and k_4 are 2 s^{-1} and $3 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$, respectively⁵.

Any attempt to record the UV/visible spectrum of HOI as a hydrolysis product of iodine in accordance with eq 1 by adjusting the pH of the solution to a range where the +1 oxidation state is dominant (i.e., at pH values from 8 to 11 where the HOI and OI^- species are metastable with respect to subsequent slower hydrolysis to yield IO_3^-) is generally thwarted by the coexistence of I_3^- , I_2 , I_2OH^- , and OI^- , all of which absorb strongly in the same spectral region.

However, by adding the solid mercarbide polymer, $[\text{Hg}_3\text{CO}(\text{ClO}_4)]_n$, to a solution of iodine in 10^{-3} M HClO_4 , the iodide ion can be effectively and rapidly scavenged from solution via an ion-exchange mechanism with the perchlorate ion (the distribution coefficient is $> 10^4$ in favor of absorbed iodide)⁶. This inorganic ion-exchange material is insoluble and has the advantage over organic resins of being insensitive to oxidation by iodine. Removal of I^- from solution drives eq 1, $\text{X} = \text{I}$, completely to the right yielding an equimolar HOI solution free of I_3^- , OI^- , or I_2OH^- interferences. As mentioned above, hypiodous acid does undergo further disproportionation as illustrated by eq 7, viz.,

such that the gradual emergence of the characteristic iodine peak at 460 nm is observed. The total equivalent iodine concentration was determined at the end of the experiment using potentiostatic coulometry. The initial spectral scan obtained after filtration could then be corrected for the known absorbance due to iodine and due to a trace amount of HgI_2 (ca. $7.5 \times 10^{-6} \text{ M}$) released from the polymer. The latter correction was ca. 15% at the absorbance maximum of HOI which occurs at 279 nm with an absorptivity of $200 \text{ M}^{-1} \text{ cm}^{-1}$. The only other published spectrum of HOI was reported in 1985 and was obtained by a very different method, but nevertheless showed good agreement with the absorption maximum recorded here, i.e., 285 nm ($200 \text{ M}^{-1} \text{ cm}^{-1}$)⁷.

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3.2.5 Construction of a Micro Raman Cell for Studying Aqueous Solutions at Elevated Temperatures and Pressures

(D. A. Palmer, F. H. Ward¹)

During the past five years numerous cell designs have appeared in the literature enabling Raman spectra of solutions to be measured at extreme conditions, typically up to 300-500°C and one kilobar pressure. These measurements are invaluable in determining speciation of the solute and have even been extended to providing approximate thermodynamic information for the equilibria involving these solutes. However, these cells are generally very bulky as they must incorporate three windows each with a complicated seal. In order to reduce the volume of solution required, the chance of seal failure, and to provide the possibility of a flow-through mode for thermally unstable solutions, the following design concept was adopted.

The schematics of this new design are illustrated in Fig. 3.14 where the dimensions are all given in inches. The unique feature of this design involves the use of a single sapphire "window" consisting of a polished sapphire cylinder .202 in. in diameter and .200 in. long, with a .0394 in. polished hole drilled down its central axis. The sapphire is sealed at both ends by gold washers acted on in turn by cylindrical titanium followers and commercial 1/16th in. stainless steel gland nuts.

Fig. 3.14. An exploded, schematic view of the Raman Cell Assembly.

This assemblage is contained in a Hasteloy B "gland body." The latter also has a .1285 in. hole to accommodate a 1/8th in. O.D. platinum RTD probe used to control the temperature of the unit and a .067 in. hole to contain a 1/16th in. K-type thermocouple used to monitor the temperature. A tapered 60° hole in the center of the gland body allows the scattered light to impinge on the lens of the monochromator. This angle can be virtually tailored to permit the maximum amount

of light to reach the lens and thereby represents a major advantage over conventional Raman cells where this angle is usually limited to the size of the seal at the exit window. A .125 in. hole is drilled through the body at right angles to the exit hole primarily to allow passage of the exiting laser beam, but also to facilitate the alignment of the cell. Surrounding the gland body is a heater core form of stainless steel which serves as a mandril for the heater element. This element is a 0.04 in. O.D. Aerocoax insulated wire (16.3 ohm/ft. at ambient temperature) with a total resistance of 50 ohms at 25°C. The heater core is encased in Macor insulation.

Pressure is supplied to this system from a HIP positive displacement pump through a manifold of 1/16th in. titanium valves and a pressure vessel containing a sealed Teflon bag. Water is pumped into this vessel compressing the bag thereby forcing the desired solution out through 1/16th in. O.D. titanium tubing welded at the other end into the titanium follower in the gland body as described above. A second length of tubing allows the solution to leave the cell via a stainless steel 1/16th in. valve secured to the manifold. The pressure is monitored at the manifold with a 0-20000 psi transducer coupled to a Precise Sensors digital indicator. The power supply and temperature control for the heater are housed within a Minco CT108 controller. The temperature can be read from a Doric digital Trendicator with a readability of $\pm 0.1^\circ\text{C}$.

Preliminary measurements have been made to 300°C and 1 kbar pressure, although it is hoped that temperatures of 500°C will ultimately be reached.

1. Plant and Equipment Division.

3.2.6 The Dissociation of Water in Sodium Trifluoromethanesulfonate Solutions to High Temperatures

(D. A. Palmer, S. E. Drummond)

Knowledge of the self-dissociation of water is fundamental to the elucidation of the

thermodynamics of hydrolysis of a solute. The dissociation quotient, Q_w , of water has been determined in two media in this laboratory, namely in NaCl¹ and KCl², at the saturation vapor pressure of water to 300°C using a hydrogen electrode concentration cell. However, for many applications, such as the complexation of certain ligands by transition metals, or the hydrolysis of reactive species such as iodine, chloride ion can be involved directly and competitively with the process under investigation. Hence, the need exists for an alternative supporting electrolyte which has the following characteristics: (1) thermally stable with respect to decomposition; (2) a strong electrolyte; (3) resistant to oxidation and reduction; (4) nonvolatile, even in acidic form; (5) incapable of significant complexation with transition metals; and (6) readily soluble in water. Sodium trifluoromethanesulfonate (or sodium triflate), NaF_3CSO_3 , which can be readily prepared by neutralization of the corresponding acid by NaOH in methanol and then recrystallized from hot methanol, appears to comply with most, if not all, of these requirements. Hence, an investigation of the ionization of water in the presence of this salt was initiated.

The concentration cell used for this purpose is a modified version of the one described in detail elsewhere³ and can be represented as follows:

In these experiments the cell was initially pressurized with three bars of hydrogen at 25°C. In this configuration the dissociation constant is obtained from the cell potential, E , by the equation,

$$\log Q_w = \log(m_2 \cdot m_3) - (F/2.3026RT) (E - E_j)$$

where the liquid junction, E_j , is estimated by application of the Henderson Equation^{1,2}. These results are summarized in Table 3.2

where it can be seen that $E_j < 1\text{mV}$ and is presumed to be estimable to within 10%, which in turn represents an uncertainty in $\log Q_w$ of < 0.002 at 25°C . (For this estimate the limiting conductances of NaCl and the sodium triflate were assumed equal).

Table 3.2. Summary of Potentiometric Results for The Dissociation Quotient of Water

t ($^\circ\text{C}$)	E (mV)	E_j (mV)	$-\log Q_w$	$-\log Q_w(\text{NaCl})$
$m_1 = 1.0078, m_2 = 0.007878, m_3 = 0.007874$				
25.0	562.25	-0.87	13.718	13.718
50.0	561.50	-0.84	12.978	12.969
75.0	563.18	-0.79	12.371	12.366
100.0	568.25	-0.78	11.891	11.872
125.0	575.46	-0.80	11.501	11.462
150.0	584.45	-0.83	11.176	11.121
175.0	595.27	-0.86	10.908	10.836
200.0	607.65 ^a	-0.88	10.684	10.608
225.0	623.20 ^a	-0.95	10.514	10.418
$m_1 = 6.4146, m_2 = 0.05084, m_3 = 0.02322$				
25.0	683.55	-0.34	14.489	14.543 ^b
50.0	691.71	-0.31	13.719	13.762 ^b
75.0	701.27	-0.30	13.082	13.097 ^b
100.0	711.35	-0.32	12.538	12.511 ^b
125.0	722.16	-0.41	12.071	11.984 ^b
150.0	734.01	-0.57	11.671	11.502 ^b
175.0	746.0 ^a	-0.81	11.314	11.056 ^b

^aExtrapolated E values to zero time to compensate for a drifting potential.

^bThese $\log Q_w$ were calculated from the general fitting equation given in reference 1.

During these experiments the potential was generally stable to within 0.1 mV for at least 15 hours, but did tend to drift to lower values at the higher temperatures as indicated in the table. This behavior may be due to decomposition of triflate ions at high tem-

peratures or to volatility of triflic acid allowing it to migrate via the vapor phase into the basic solution. The former is unlikely in light the results of a kinetic study⁴ of this process conducted at temperatures above 300°C . The underlying cause of the drifting potential is still under investigation.

A comparison of the $\log Q_w$ values for sodium triflate and sodium chloride in 1m salt solution shows them to be indistinguishable at lower temperatures with meaningful differences emerging above 100°C . At the higher ionic strength the differences appear substantial; however, this may be due largely to uncertainties in the NaCl values obtained by extrapolation of the measurements above their three molal limit. It is interesting to note that at unit ionic strength the $\log Q_w$ values in KCl are -13.753 ± 0.006 at 25°C and -10.490 ± 0.021 at 225°C so that, at least at this molality, sodium triflate solutions show values intermediate between the two chloride solutions.

Upon completion of more experiments at other ionic strengths the $\log Q_w$ values will be subjected to the usual least-squares analysis which includes functions of temperature and ionic strength, as well as allowance for the activity coefficients of H^+ and OH^- , and the activity of water in terms of the Debye-Hückel expansion.

These experiments clearly demonstrate the potential of NaCF_3SO_3 as a non-complexing electrolyte and plans are being made to utilize this feature in studies of metal ion complexing in both potentiometric and solubility studies.

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2. F. H. Sweeton, R. E. Mesmer, and C. F. Baes, Jr., J. Solution Chem. **3**, 191 (1974).
3. R. E. Mesmer, C. F. Baes, Jr., and F. H. Sweeton, J. Phys. Chem., **74**, 1937 (1970).
4. L. Fabes and T. W. Swaddle, Can. J. Chem., **53**, 3053 (1975).

3.2.7 Modified Raoult's Law and the Solvent Structural Constant Applied to Organic-Water Systems¹

(W. L. Marshall)

Previously, support was presented for applying a universal solvent structural constant (B) in describing the activity of water for aqueous electrolyte solutions^{2,3}. This constant was found to be essentially independent of temperature (25 - 300°C) but to decrease moderately in concentrated solutions. The composition of free water was represented by absolute concentration or by mole fraction. The concentration (or mole fraction) of free water was obtained by subtracting the number of moles of water believed to solvate the solute species. The extent of solute association (or ionization) also needed to be considered.

With the use of mole fraction we defined this procedure as the modified Raoult's law approach, and we have now applied this approach to the description of a small-sized non-linear organic molecule (urea) dissolved in water. Insignificant ionization occurs for urea, and the extent of solvation is expected to be small. For no (or insignificant) ionization of a solute the mole fraction of free water may be written,

$$N_1^w = \frac{[55.51/B - G/B \cdot m]}{[55.51/B - G/B \cdot m + m]} \quad (1)$$

or

$$N_1^w = \frac{[55.51 - G \cdot m]}{[55.51 - G \cdot m + B \cdot m]} \quad (2)$$

where G is the average solvation number of the solute, the value, $(55.51/B - G/B \cdot m)$, represents the number of moles of free water in 1000 g (55.51 moles H₂O) of total water, and m is the molality of solute (or number of moles dissolved in 1000 g of total water).

The MRL expression is thus represented³,

$$a(\text{H}_2\text{O}) = [N_1^w]^{1/B} \quad (3)$$

From the previous work, B is defined as the solvent structural constant and is believed to equal 6.67 for aqueous electrolyte solutions of moderate molalities (0 - 2m). The previous studies^{2,3} indicated that at low concentrations of electrolyte B has the value near 6.67. It may be defined as an average number of significant molecular interactions between solvent molecules for a given solvent molecule. These interactions must therefore be broken upon vaporization, and thus B can be related to both a structural property and the number of interactions or "bonds" broken in the vaporization process, as represented by eq. (3).

Figures 3.15 and 3.16 show that an aqueous organic system containing as a solute the small sized, non-linear urea molecule is well described by the single solvation parameter, G_F [where the subscript F refers to an average value over a full (or wide) range of molality]. For Fig. 3.15, eq. (2) was applied in solving for G_F with the use of a series of separate values of B. The average percent deviation in the calculated values of $a(\text{H}_2\text{O})$ from those obtained from smoothed, experimental osmotic coefficients⁴ at 25°C and from 0 to 20 m urea are plotted against B to show the steep sides of the plot in reaching a minimum at B equal to 6.80, with G_F equal to 1.63. In Fig. 3.16, the values of $a(\text{H}_2\text{O})$ obtained from experiment are plotted against the calculated values of the modified Raoult's law expression given by eq. (3). A value for B of 6.67 was used for this plot since (i) this value has been proposed to be universal for water containing moderate concentrations of solute^{2,3}, (ii) the best fit value from Fig. 3.15 is very close (within 2%) to this value, and (iii) the average deviation in fit of 0.09% in $a(\text{H}_2\text{O})$ is essentially the same as that for the best

Fig. 3.15. The Average Deviation [in % $a(\text{H}_2\text{O})$] versus B for the Description of the Activity of Water [$a(\text{H}_2\text{O})$] for Aqueous Urea Solutions at 25°C by the Modified Raoult's Law Model.

Fig. 3.16. A Plot of the Activity of Water [$a(\text{H}_2\text{O})$] for Aqueous Urea Solutions at 25°C versus the Modified Raoult's Term, $[N_1^*]^{1/B}$, Showing the Excellent Agreement from 0 to 54.6 Wt. % with the Single Solvation Parameter (G_F) and Use of the Previously Proposed Universal Value for B (6.67).

fit from Fig. 3.15. A best fit value near 6.67 to the high molalities for the aqueous urea solutions is in contrast with the decrease to about 5.5 observed for the description of the concentrated aqueous electrolytes. The simple, non-ionized urea solute may not decrease noticeably the "bonding structure" of water as might be caused by high molalities of ions. Thus the description of a simple organic-water system by the modified Raoult's approach would appear to provide additional validity for this model.

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4. G. Scatchard, W. J. Hamer, and S. E. Wood, J. Amer. Chem. Soc., 60, 3061 (1938).

4. GEOCHEMISTRY

This program has research efforts in three interrelated disciplines: igneous petrology (4.1), hydrothermal geochemistry (4.2), and stable isotope geochemistry (4.3). The principal contributions of this program have come from experimental studies using a wide array of unique equipment. In the past year, however, a significant portion of this program has been devoted to field studies in volcanic terranes of California and New Mexico and in crystalline rocks of the southern Appalachians. This temporary focus on field projects was motivated by opportunities to play an important role in the Continental Scientific Drilling Program and to broaden our scope through collaboration with field geologists. Our experimental program has been stimulated by these recent field studies and continues with the essential goal of understanding geological processes by integrating fundamental data from experimental studies with accurate physical and chemical models.

4.1 High Temperature Silicate Geochemistry

Results of controlled oxygen fugacity experiments conducted to investigate iron redox kinetics in silicate liquids were reported in the last annual report. An important observation made in the experimental study was that redox changes in rhyolite liquids are very sluggish compared with basalt and andesite liquids. This observation leads to the hypothesis that glassy rhyolites may preserve the pre-eruption redox signature of rhyolite magmas.

During the past year, two DOE-sponsored Continental Scientific Drilling Program (CSDP) projects have provided core samples of complete sections through obsidian flows at Inyo Domes, CA, and Valles Caldera, NM. These core materials have provided a unique opportunity for investigating rhyolite eruption processes through measurement of chemical variations within a glassy rhyolite flow unit and the associated feeder conduit. These samples permit initial testing of the hypothesis developed during experimentation at ORNL. The hypothesis would predict that the oxidation state of glassy rhyolites is unchanged from that of their magmatic precursor, and that fresh glasses within a flow unit should have the same oxidation state regardless of position within the flow.

Bulk ferrous-ferric analyses have been completed for representative suites from both DOE drilling projects. The results presented below indicate that apparently unaltered glasses from the flow top, bottom and interior have the same

oxidation state, and therefore provide a tentative confirmation of the hypothesis.

4.1.1 Fe^{3+} - Fe^{2+} Variations in Rhyolite Lavas. (M. T. Naney, S. E. Swanson¹)

Core samples from four CSDP holes recently completed at Inyo Domes, CA, and Valles Caldera, NM, have been analyzed by a microcolorimetric method for Fe^{2+} and total Fe content. The broad range of $\text{Fe}^{2+}/\text{Fe}(\text{tot})$ values measured indicates that rocks from different portions of the flows and feeder conduits samples have experienced varying degrees of oxidation. The pattern of oxidation is systematic and can be related to the subsolidus cooling history.

Fresh glasses from flows (tops-interiors-bottoms) and the dike margin from Inyo Domes all have similar $\text{Fe}^{2+}/\text{Fe}(\text{tot})$ values - 0.62 to 0.75 (Fig. 4.1). In addition, rapidly quenched tephra glasses that are contemporaneous with the Inyo Domes core samples have essentially the same value - 0.74. Materials with lower $\text{Fe}^{2+}/\text{Fe}(\text{tot})$ values have experienced varying degrees of oxidation during subsolidus devitrification. The flow interiors and bulk of the feeder dike materials sampled are crystalline and have microscopic textures that are consistent with subsolidus crystallization. These rocks have $\text{Fe}^{2+}/\text{Fe}(\text{tot})$ values that cluster near 0.50 (Figs. 4.1 and 4.2). The most oxidized $\text{Fe}^{2+}/\text{Fe}(\text{tot})$ values (approximating 0.15) (Fig. 4.2) were observed in samples of lithophysae. These materials are produced in the flow interior adjacent to areas of spheru-

Fig. 4.1. Variation of the ferrous to total iron ratio $[\text{FeO}/\text{FeO}(\text{tot})]$ and rhyolite textures with depth in CSDP corehole RDO-2a, Obsidian Dome, Long Valley, CA. The following abbreviations are used in the stratigraphic column: ves = vesicular; lithophys = lithophysae. Solid and cross-hatched bars indicate fresh glassy rhyolite and crystalline rhyolite, respectively.

litic crystal growth. The interiors of the spherulites are commonly hollow and were most probably occupied by an aqueous fluid that promoted oxidation of the spherulite and adjacent material during subsolidus cooling.

The uniform $\text{Fe}^{2+}/\text{Fe}(\text{tot})$ values of what appear to be fresh glassy rocks that have experienced different cooling histories at Inyo Domes (flow tops-interiors and bottoms; conduit dike margin; and air fall tephra) are consistent with the hypothesis developed from experiment:

Fig. 4.2. Variation of the ferrous to total iron ratio $[\text{FeO}/\text{FeO}(\text{tot})]$ and rhyolite textures with depth in CSDP corehole VC-1, Banco Bonito Obsidian, Valles Caldera, NM. The following abbreviations are used in the stratigraphic column: litho = lithophysal; vitro = vitrophyre; porph = porphyritic. Solid bars indicate composition of "glassy" rhyolites. Cross-hatched and stippled bars indicate obviously devitrified and oxidized samples.

studies of iron redox kinetics in silicate melts. In general, rocks sampled from the Banco Bonito obsidian section of the Valles Caldera corehole have experienced significant oxidation compared to the Inyo Domes samples (Fig. 4.2). This is reflected in the $\text{Fe}^{2+}/\text{Fe}(\text{tot})$ values measured, the H_2O contents (0.3 to 0.6 wt pct H_2O) of samples measured by

H. R. Westrich (SNL), and petrographic observation. Despite the pervasive oxidation observed in core samples, surface outcrop samples of the Banco Bonito obsidian have $\text{Fe}^{2+}/\text{Fe}(\text{tot})$ values similar to those of fresh glass samples at Inyo Domes - 0.62 to 0.71. These are the highest values observed in the suite of Banco Bonito samples measured and may represent relatively unaltered material that reflects the pre-eruption f_{O_2} conditions in the magma chamber.

1. University of Alaska.
2. H. R. Westrich, personal communication.

4.1.2 Origin of Microlites in Rhyolite: An Example from Inyo Domes, California

(M. T. Naney, S. E. Swanson,¹ H. R. Westrich²)

Microlites having an average length of 7 to 10 μm are a ubiquitous constituent of obsidians from the CSDP coreholes drilled at Inyo Domes, CA. SEM/EDX studies suggest that the microlites are dominantly biotite and hornblende with tabular and skeletal habits.

Statistical analysis of the size distribution of microlites does not show any significant ($\alpha = 0.99$) difference between samples cooled relatively quickly (at the base or distal portions of the obsidian flow) and those cooled more slowly (in the flow interior or near the vent). This suggests that crystallization of the microlites is independent of the post-eruptive cooling history and that the microlites crystallized prior to eruption of the obsidian.

Other lines of evidence are consistent with the pre-eruption crystallization of the microlites. (1) Air-fall tephra represent the earliest eruption products of the Inyo system, and glass from these tephra contains microlites. The H_2O content (1.5 wt pct) of White Wing tephra glass erupted from the Glass Creek vent is higher than that of contemporaneous, but post-tephra, massive obsidian erupted 1.5 km north at Obsidian Dome (0.1 wt pct), suggesting that the tephra glass represents quenched, un-degassed magma. The presence of microlites in this H_2O -rich tephra glass is

consistent with pre-eruption crystallization. (2) In the flow interior, microlite-defined flow banding is cut by devitrification textures that are related to the post-eruptive cooling of the obsidian. (3) The presence of hydrous phase microlites is consistent with crystallization from a hydrous melt³ and is not expected at the surface. (4) Crystallization of biotite and/or hornblende without plagioclase, sanidine, or quartz is not consistent with equilibrium crystallization from low H_2O (e.g., 0.1 wt pct) melts³ but is consistent with non-equilibrium crystallization at moderate to high undercooling.⁴ These observations from natural obsidians and from experiments suggest that the microlite assemblages crystallized prior to surface extrusion under nonequilibrium conditions in response to moderate or high undercooling. A likely mechanism to produce the necessary undercooling is the melt compositional change accompanying the onset of degassing.

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2. Sandia National Laboratory.
3. M. T. Naney, *Am. J. Sci.* **283**, 993 (1983).
4. M. T. Naney, Ph.D. Thesis, Stanford University, 229 p. (1978).

4.1.3 Sample Manipulator and Quenching Apparatus for High Temperature, 1 atm Experiments (M. T. Naney, F. H. Ward¹)

A self-aligning, guide-track apparatus has been adapted to a vertical-tube gas-mixing furnace for use in sample loading and quenching of high temperature, 1 atm experiments. This apparatus facilitates experimentation with materials that cannot - or should not - be attached to a platinum wire-loop.

Platinum wire-loops are widely used in 1 atm investigations of silicate melt equilibria and crystallization as crucible/sample holders. The use of platinum-loops maximizes sample/furnace-atmosphere interaction, while minimizing loss of iron from the sample to the wire "crucible." However, several problems are encountered during operations that require

moving samples in and out of the small-bore of the vertical-tube furnace. These include: (1) accidental contact of samples with the hot furnace wall during insertion, positioning, or withdrawal maneuvers; (2) accidental contact of samples with the zirconia oxygen-sensor which is normally in the hot zone of the furnace (such contact can result in sample loss, and more unfortunately, contamination and subsequent malfunction of the sensor); and (3) poor adhesion of some types of samples to the platinum wire-loops, making them prone to falling off the wire when lowered into the furnace.

A simple accessory helps to alleviate these difficulties by permitting rapid and precise sample insertion, manipulation, and withdrawal. This apparatus (Fig. 4.3) is designed to be used with water-cooled furnace end-caps built

according to the design described by Williams and Mullins.² The apparatus is especially advantageous when experiments involve the use of starting materials that do not adhere well to a platinum wire. In this circumstance, samples can be successfully lowered into the furnace by simply laying them on top of the platinum wire-loop prior to insertion into the furnace. The guide track permits precise, controlled vertical movement of the sample support rod and attached platinum wire-loop so that non-adhering samples remain atop the platinum loop. This capability was found to be particularly useful for a study in which short cylinders of obsidian were used as starting materials.

In summary, the advantages to be gained by using a guide track assembly in high temperature, 1 atm experimentation are: (1) ease and

Fig. 4.3. Design details of the sample manipulator/quenching apparatus. Dimensions are in centimeters unless otherwise indicated. Dimensions in parentheses are the inch equivalents. (a) Section view of guide track and attached base plate. (b) Plan view of base plate showing attached guide track and position of sample rod collar. (c) Section view of sample rod collar. (d) Plan view of sample rod clamp.

speed of insertion, manipulation, and withdrawal of samples; and (2) handling of "difficult" or special samples that are not secured to the platinum wire-loop prior to experimentation.

1. P&E Division, ORNL.
2. R. J. Williams and O. Mullins, NASA Tech. Memo 58234 (1981).

4.1.4 Sulfur Mobility in Silicate Melts

(D. R. Cole, M. T. Naney, E. M. Ripley¹)

An understanding of the solubility and mobility of sulfur in silicate melts is of critical importance in any attempt to quantify processes influencing the evolution of igneous rocks such as the exsolution of volatiles (e.g., SO_2 , H_2S , etc.) during magma emplacement (at depth or at the surface) or the formation of magmatic sulfide ore deposits. At present, there is little information on the solubility of sulfur in magmas, and even less regarding the mobility of sulfur as a function of the parameters most influential in the genesis of magmas, i.e., temperature, pressure, oxidation state, and composition. The results presented below are of a preliminary nature, and further research is in progress.

The rates of sulfur mobility were investigated in liquidus experiments using a natural troctolite (approximates an olivine tholeiite basalt) obtained from the Duluth Complex, Minnesota. Desorption experiments were performed at 100 kPa (1 atm), temperatures of 1200 and 1300°C and $\log f_{\text{O}_2}$ values appropriate for QFM or Ni-NiO at these two temperatures (i.e., -7.25 and -8.3, QFM at 1300 and 1200°C, respectively; and -6.5 and -7.6, Ni-NiO at 1300 and 1200°C, respectively). After heating in a CO_2/CO furnace atmosphere for periods ranging from 60 to 1440 minutes, samples were withdrawn from the furnace and quenched in a filtered H_2/Ar gas jet. Sulfur analyses were performed using the Leco-Sulfur Analyzer. The initial sulfur concentration in the troctolite is 2.5 ± 0.05 wt. %.

The systematic changes in sulfur concentration in the quenched glass as a function of time are shown in Figure 4.4. These data indicate that sulfur desorption is an extremely rapid process, wherein over 90% of the total sulfur in the troctolite (originally as iron or copper sulfides) is lost during the first few hours of heating. In all cases, the magnitude of sulfur loss is greatest at the higher temperature conditions. At longer times, in excess

Fig. 4.4. Sulfur concentration (ppm) in quenched glasses plotted as a function of reaction time (days) for troctolite melting experiments. The initial sulfur content of the troctolite is 2.5 ± 0.05 wt. %.

of about four hours, the rate of sulfur loss becomes much less rapid.

This trend of rapid sulfur loss followed by a slow loss is similar in many respects to the rates of change of $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratios versus time for basalt described by Naney and Swanson.² They observed a rapid increase in $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratios within the first few hours followed by a steady state behavior, where the initial slopes and hence fastest rates are greatest at lower f_{O_2} values. Because of the limited number of data, it is difficult to quantitatively relate variations in sulfur content to the differences in oxidation state. In general, there is a tendency for the amount of sulfur desorbed at 1300°C and $\log f_{\text{O}_2} = -7.3$ to exceed the amount of sulfur lost at $\log f_{\text{O}_2} = -6.5$. At 1200°C,

the reverse is observed where the sulfur contents for the low f_{O_2} (-8.3) case exceed those sulfur values for the high f_{O_2} (-7.6) condition. These differences, however, are commonly within the analytical error of the sulfur analyses, which at concentrations below about 500 ppm is on the order of 10%.

We have modeled the variations in sulfur content as a function of time assuming the concentration-time trends resulted from diffusion of some, as yet unidentified, sulfur species in a spherical liquid silicate drop. The boundary conditions assumed most appropriate for these experiments are: (1) the concentration of diffusing species at the surface is constant and in equilibrium with the f_{O_2} of the CO_2/CO furnace atmosphere; (2) samples have a uniform initial concentration of diffusing component; and (3) the diffusion coefficient $\bar{D}$ at constant temperature is independent of the diffusing component. Two numerical approaches were used; one described by Barrer and Brook³

$$\frac{C_i - C_m}{C_i - C_\infty} = \frac{2A}{V} \left(\frac{\bar{D}}{\pi} \right)^{1/2} \sqrt{dt}$$

where C_m is the mean concentration at some time t , C_i is the initial uniform concentration, C_∞ is the limiting concentration at equilibrium (infinite time), A is the surface area of the specimen ($\sim 0.503 \text{ cm}^2$ for a drop with a 0.2 cm radius) and V is its volume.

A second model described by Crank⁴ for a sphere was used

$$\frac{C_i - C_m}{C_i - C_\infty} = 1 - \sum_{n=1}^{\infty} \frac{6\beta(\beta+1)\exp(-\bar{D}q_n^2 t/a^2)}{9 + 9\beta + q_n^2 \beta^2}$$

where the q_n 's are the non-zero roots of

$$\tan q_n = 3q_n / (3 + \beta q_n^2)$$

and

$$\beta = 3V/4\pi a^3$$

which is the ratio of the volumes of atmosphere in the hot zone of the furnace and sphere (of

radius a). Solving for $\bar{D}$ in both expressions and using the mean sulfur concentrations at 1200 and 1300°C (i.e., combined data at different f_{O_2}), we get diffusion coefficients shown in Figure 4.5. The Barrer and Brook³ method produced slightly lower diffusivities compared to the Crank⁴ method, i.e., $10^{-5.84}$ versus $10^{-5.69}$ and $10^{-5.17}$ versus $10^{-5.32} \text{ cm}^2/\text{sec}$ at 1200 and 1300°C, respectively. However, both approaches yield an identical activation energy of 54.8 kcal/mol which is similar to the value of 49 kcal/mol obtained by Saito and Kawai⁵ for sulfur diffusion in $CaO-Al_2O_3-SiO_2$ slags. The overall magnitudes of diffusion calculated from our study are appreciably higher than the Japanese data due in large part to the great difference in melt compositions used in each study. Additionally, our rates are about three

Fig. 4.5. Ranges of experimental diffusivities ($\bar{D}$) of sulfur in troctolite melts compared against diffusivities of sulfur as well as other components in a variety of compositions. O refers to the Crank⁴ method of calculating $\bar{D}$, Δ refers to the Barrer and Brook³ method, using experimental data shown in Figure 4.4. Saito and Kawai⁵ determined $\bar{D}$ values for sulfur in $CaO-Al_2O_3-SiO_2$ slags. Turkdogan and Pearce⁶ obtained sulfur diffusivities in $CaO-SiO_2$ melts; Shaw⁷ measured rates of H_2O diffusion in obsidian, and Drury and Roberts⁸ measured H_2 rates in silica glass. The $\bullet$ refers to data from Buchanan and Nolan.

orders of magnitude greater than diffusivities calculated from the Stokes-Einstein relation

$$\bar{D} = kT/(6\pi\eta r)$$

where k is the Boltzmann constant, T is temperature (K), η is the melt viscosity, and r is the hard sphere radius of a "noninteracting, neutral species." Clearly, the Stokes-Einstein approach is unacceptable in determining diffusion coefficients, but it is rather good at predicting activation energies (56.2 predicted versus 54.8 kcal/mol experimental). Our data at 1200°C are also about two orders of magnitude greater than data given by Buchanan and Nolan⁶ obtained from sulfur uptake experiments with basalt. This much difference in rates between the sorption and desorption of sulfur seems unreasonably large, but further experimentation is necessary to demonstrate this.

1. Indiana University.
2. M. T. Maney and S. E. Swanson, *Contrib. Mineral. Petrol.* (in press).
3. R. M. Barrer and D. W. Brook, *Trans. Faraday Soc.* **49**, 1049-1059 (1953).
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5. T. Saito and Y. Kawai, *Sci. Rept. Inst. Tokoku Univ., Japan* **5**, 460-468 (1953).
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8. H. R. Shaw, *Carnegie Inst. of Wash., Publ.* **634**, *Geochemical Transport and Kinetics*, 139-170 (1974).
9. T. Drury and J. P. Roberts, *Phys. Chem. Glasses* **4**, 79-90 (1963).

4.2 Hydrothermal Geochemistry

4.2.1 The Effect of Transport and Deposition on Ag/Au Ratios in Hydrothermal Solutions

(D. R. Cole, S. E. Drummond)

A thermodynamic model^{1,2} has been used to quantify the effects of transport and deposi-

tion on the gold and silver contents, Ag/Au ratios and $\Sigma\text{CO}_2/\Sigma\text{H}_2\text{S}$ ratios in boiling hydrothermal solutions. Boiling is singled out because many geothermal systems and their "fossil" ore deposit equivalents exhibit some evidence of two-phase behavior. A total of 360 transport calculations were carried out for the following conditions: $T = 150^\circ - 300^\circ\text{C}$, $\text{Cl}^- = 0.1$ and 1.0 m, $\text{pH} = 4-6$, $\Sigma\text{H}_2\text{S} = 0.1 - 10^{-5}$ m, and $\Sigma\text{H}_2\text{S}/\Sigma\text{SO}_4 = 10 - 109$. Of these, we chose 54 to use as initial conditions in the boiling calculations, which focused on the influence of temperature, ΣCO_2 , $\Sigma\text{H}_2\text{S}$, and pH on chemical shifts and accompanying mineral deposition during progressive vaporization. These calculations were constrained by selecting an open rather than a closed system to simulate boiling. Here, open implies the liquid is vaporized progressively such that each increment of vapor is removed from contact with the liquid as it forms. Additionally, we opted for the simplicity of isothermal rather than isenthalpic boiling.

Specifically, we addressed the following questions:

- (1) Under what conditions are gold and silver best transported?
- (2) What is the range of Ag/Au ratios expected in solution prior to the boiling event?
- (3) Upon boiling, what changes take place in the Ag/Au ratios, and why?
- (4) What sequence of gold-silver mineralization (zoning) can be expected under different initial conditions of boiling (e.g., high pH versus low pH; high CO_2 versus low CO_2)?
- (5) Under what conditions should we expect the highest grades of gold and silver in systems affected by boiling?

The modeling results strongly suggest that the chemical and mineralogical trends observed in many geothermal systems and epithermal ore deposits may be directly related to the transport properties of gold and silver, and the properties of precious-metal bearing solutions undergoing boiling. The following list is intended to highlight the major chemical trends observed in this modeling study.

1. The $\text{Au}(\text{HS})_2^-$ complex dominates at moderate to high $\Sigma\text{H}_2\text{S}$ and pH, high $\Sigma\text{H}_2\text{S}/\Sigma\text{SO}_4$, and low to moderate temperature. These conditions favor low Ag/Au ratios in solution and argentite as the dominant silver phase (see Fig. 4.6).
2. The AuCl_2^- complex dominates at low $\Sigma\text{H}_2\text{S}$, low to moderate pH, low $\Sigma\text{H}_2\text{S}/\Sigma\text{SO}_4$, and high temperature. These conditions favor high Ag/Au ratios in solution and generally native silver as the most stable silver phase, although argentite can also be important (see Fig. 4.6).

Fig. 4.6. The stability boundaries (equal concentration) between the two dominant gold complexes, $\text{Au}(\text{HS})_2^-$ and AuCl_2^- represented in $\Sigma\text{H}_2\text{S}$ versus pH space for two chloride concentrations (0.1 and 1.0 m). The stability boundaries for the solid silver phases, argentite (Ag_2S) and native silver (Ag^0) are also shown. The two plots were constructed with a $\Sigma\text{H}_2\text{S}/\Sigma\text{SO}_4$ ratio of 10.

3. The overall frequency distribution of the Ag/Au ratios in solution exhibits many similarities with the patterns given for natural systems. Collectively, these distributions display a pronounced mode between Ag/Au values of 10 and 100.
4. The depth at which boiling commences becomes shallower with either decreasing temperature and/or CO_2 concentration for a constant salinity (see Fig. 4.7). The depth to the top of the mineralized boiling interval is controlled principally by the

Fig. 4.7. The trends in metal enrichment (ppm/meter), Ag/Au ratios deposited and $\Sigma\text{CO}_2/\Sigma\text{H}_2\text{S}$ as a function of depth for open, isothermal boiling. The initial conditions modeled are $\Sigma\text{CO}_2 = 1.0$ m, $\Sigma\text{H}_2\text{S} = 0.001$ m, $\Sigma\text{SO}_4 = 10^{-5}$ m, $\text{Cl}^- = 1.0$ m, and pH = 5 for 300°, 250°, and 200°C. The depths have been calculated assuming a pressure gradient of 175 bars/km. The tick marks and numbers across the top of each figure refer to percent boiling. The stability fields for the silver phases, argentite (Ag_2S) and native silver (Ag^0), and gold complexes AuCl_2^- (referring to $\text{AuCl}_2^- > \text{Au}(\text{HS})_2^-$), and $\text{Au}(\text{HS})_2^-$ (referring to $\text{Au}(\text{HS})_2^- > \text{AuCl}_2^-$) are also shown. The cumulative percent of metal deposited is indicated as follows: ■ 90% gold, □ 50% gold, ● 90% silver, ○ 50% silver. Gold —, silver ····, Ag/Au deposited ----, $\Sigma\text{CO}_2/\Sigma\text{H}_2\text{S}$ - - -.

liquid-vapor properties of the $\text{NaCl-H}_2\text{O}$ system since most of the gases exsolve early in the boiling process (particularly for open systems). Therefore, solutions with the highest initial gas concentrations will tend to deposit gold and silver over the greatest vertical distances, and produce deposits with lower ore grades. These relationships are observed in several geothermal and ore deposit systems.

5. The modeling indicates that the magnitudes of precious metal enrichment remain relatively constant as a function of depth, except near the top of the mineralized boiling interval. In this region, the model predicts the presence of more intense zones of metal enrichment which may be analogous to the very high-grade bonanza ores observed in many precious metal ore deposits (see Fig. 4.7).
6. The fact that the absolute magnitudes of metal enrichment resulting from boiling are very low indicates that many volumes of a boiling fluid passing through a given volume of rock are required in order for ore grades in the boiling zone to reach levels typical of most epithermal deposits.
7. The Ag/Au ratios based on the amounts of metal lost from solution exhibit changes during the boiling process that are typically less than one order of magnitude. These ratios remain relatively constant throughout much of the boiling process, but do undergo marked change near the top of the mineralized boiling interval. Significant increases in Ag/Au ratios are associated with systems that have moderate to high temperature and pH, low $\Sigma\text{H}_2\text{S}$, and generally high $\Sigma\text{CO}_2/\Sigma\text{H}_2\text{S}$ ratios. Gold and silver are transported principally as chloride complexes at these conditions. Conversely, a drop in Ag/Au ratios near the top of the boiling zone accompanies systems with low to moderate temperature, moderate to high pH, high $\Sigma\text{H}_2\text{S}$, and low $\Sigma\text{CO}_2/\Sigma\text{H}_2\text{S}$. Gold is transported dominantly as $\text{Au}(\text{HS})_2^-$ at these conditions.
8. The frequency distribution of the boiling Ag/Au ratios is very similar to both the transport histogram and the histograms given for natural deposits. The high Ag/Au mode of 10 to 100 is preserved, and the overall range of Ag/Au values is basically the same.
9. The model predicts that $\Sigma\text{CO}_2/\Sigma\text{H}_2\text{S}$ ratios will decrease continuously with decreasing depth for all boiling conditions. As the result of exsolution of CO_2 and H_2S , the near-surface environment of many boiling systems may undergo extensive acid alteration.
10. Metal zoning resulting from boiling can be divided into two general categories; enrichments of either gold or silver in the sequence overlying a zone of base metal sulfides. The former case is associated with low to moderate temperature boiling systems whose solutions have initially high $\Sigma\text{H}_2\text{S}$, moderate to high pH, and generally low $\Sigma\text{CO}_2/\Sigma\text{H}_2\text{S}$. These conditions (i.e., small vertical extent) result in the highest gold grades for boiling systems.

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4.2.2 Hydrothermal Crystal Growth in the Form of Layers from Solution or Melt - A Modeling Approach

(D. R. Cole)

In recent years, it has become quite apparent that for many geochemical systems, kinetics is the controlling factor in determining their evolution and ultimate fate. The evidence for time-dependent behavior is preserved in rocks in the form of elemental and isotopic zoning, and textural variations. It is clear that mineral growth and/or dissolution play a major role in controlling the physical and chemical variations in rocks, and that a

detailed understanding of mineral growth kinetics is required in order to quantify important crustal processes such as vein deposition in geothermal systems and crystallization in silicate melts.

The purpose of this investigation is to evaluate the growth rates of crystals (planar for simplicity) from either solutions or melts for a linear rate of cooling.¹ For a planar crystal growing into an infinite body of solution, the differential equation governing diffusion without convection is

$$D \frac{\partial^2 C}{\partial y^2} + r_f \frac{\partial C}{\partial y} = \frac{\partial C}{\partial t}$$

where D is the diffusion coefficient of the solute in solution or melt, C is molar concentration, y is the distance into the solution from the crystal surface, and r_f is the flow rate of solution into the crystal surface due to growth (the crystallization flow). For liquid mixtures, the partial molar volume $\bar{V}$ of solute is assumed to be constant, and if no solvent is present in the crystal, then r_f is related to the linear growth rate by

$$r_f = r_g \bar{V} C_s$$

where C_s is the solute concentration in the crystal (mol/cm^3) and r_g is the crystal growth rate. In order to solve for r_g , we must satisfy both a material balance and a finite interfacial kinetic relationship at the crystal surface

$$r_g = \psi_i (C_i - C_e) = \frac{D(\partial C/\partial y)_0}{C_s(1 - \bar{V}C_i)}$$

where ψ_i is the linear interfacial rate constant, C_i is the solute concentration at the interface and C_e is the equilibrium concentration (solubility) at temperature T , which is taken to be a linear function of time.

At time = 0, the solution (or melt) is assumed to be homogeneous at concentration C_0 ,

corresponding to the solubility at the initial temperature, T_0 . Very far from the crystal, the concentration C_∞ remains at C_0 . A finite difference solution was used to calculate the changes in concentration^{1,2} in solution (melt) as growth proceeds by assuming that these changes take place only near the crystal surface, out to a distance on the order of several $(Dt)^{1/2}$. The model requires data on the diffusion coefficient, solubility, molar volume in solution (or melt) and interfacial kinetics as a function of temperature. Because the model can evaluate only simple polymeric species in solution, we investigated the growth rate of quartz from hydrothermal solutions and a silicic melt. Preliminary results are presented in Figs. 4.8 and 4.9 for these two systems, respectively.

For the quartz-water system, rate constants for precipitation given by Rimstidt and Barnes³ were recast to interfacial kinetic constants ($10^{-8} - 10^{-5} \text{ cm}^4/\text{mol}\cdot\text{sec}$). Curves A (250°C), C

Fig. 4.8. Calculated growth rate of quartz versus time for different hydrothermal conditions. A: $T = 250^\circ\text{C}$, $-dT/dt = 0.5 \text{ K/hr}$, $\psi_i = 10^{-8} \text{ cm}^4/\text{mol}\cdot\text{sec}$, $D = 10^{-5} \text{ cm}^2/\text{sec}$; B: $T = 250^\circ\text{C}$, $-dT/dt = 2.5 \text{ K/hr}$, $\psi_i = 10^{-8} \text{ cm}^4/\text{mol}\cdot\text{sec}$, $D = 10^{-5} \text{ cm}^2/\text{sec}$; C: $T = 350^\circ\text{C}$, $-dT/dt = 0.5 \text{ K/hr}$, $\psi_i = 10^{-8} \text{ cm}^4/\text{mol}\cdot\text{sec}$, $D = 10^{-5} \text{ cm}^2/\text{sec}$; D: $T = 350^\circ\text{C}$, $-dT/dt = 2.5 \text{ K/hr}$, $\psi_i = 10^{-8} \text{ cm}^4/\text{mol}\cdot\text{sec}$, $D = 10^{-5} \text{ cm}^2/\text{sec}$; E: $T = 150^\circ\text{C}$, $-dT/dt = 0.5 \text{ K/hr}$, $\psi_i = 10^{-6} \text{ cm}^4/\text{mol}\cdot\text{sec}$, $D = 5 \times 10^{-5} \text{ cm}^2/\text{sec}$.

Fig. 4.9. Calculated growth rate of quartz versus time for a silicic melt (granitic in composition). F: $T = 700^\circ\text{C}$, $-dT/dt = 0.2$ K/hr, $\psi_i = 0.1$ cm⁴/mol³·sec, $D = 10^{-5}$ cm²/sec; G: $T = 700^\circ\text{C}$, $-dT/dt = 0.5$ K/hr, $\psi_i = 0.1$ cm⁴/mol³·sec, $D = 10^{-5}$ cm²/sec; H: $T = 700^\circ\text{C}$, $-dT/dt = 0.5$ K/hr, $\psi_i = 0.1$ cm⁴/mol³·sec, $D = 10^{-5}$ cm²/sec; I: $T = 700^\circ\text{C}$, $-dT/dt = 2.5$ K/hr, $\psi_i = 0.1$ cm⁴/mol³·sec, $D = 10^{-5}$ cm²/sec; J: $T = 700^\circ\text{C}$, $-dT/dt = 0.5$ K/hr, $\psi_i = 0.1$ cm⁴/mol³·sec, $D = 10^{-6}$ cm²/sec. An activation energy for solubility of ~ 20 kcal/mol was used for curves F, G, I, J; a E_{act} of 30 kcal/mol was used for curve H.

(350°C) and E (150°C) correspond to conditions where the cooling rate ($-dT/dt$) was 0.5 K/hr and $D = 10^{-5}$ cm²/sec, solubilities and molar volumes were taken from Walther and Helgeson, 4 and diffusion coefficients were estimated from the Stokes-Einstein relation ($\sim 10^{-4}$ to 10^{-5} cm²/sec). A cooling rate of 2.5 K/hr was used for curve B (250°C, $D = 10^{-5}$ cm²/sec), whereas a $D = 5 \times 10^{-5}$ cm²/sec was used for curve D (250°C, $-dT/dt = 0.5$). These trends indicate that the growth rate, r_g , is nearly proportional to time and increases with increasing temperature (which also increases the solubility and ψ_i). For larger cooling rates (B), the r_g versus t trend exhibits a pronounced curvature for longer times (>100 hr) as the rate of change of solubility begins to diminish. Finally, a change in the diffusion coefficient has nearly no effect on the growth

rate of quartz (curves A and D), implying that for the conditions modeled, interfacial kinetics is rate-limiting.

These results are in stark contrast to those shown in Fig. 4.9 for quartz growth in a silicic melt. For these calculations, we assumed that: (1) the average solubility of quartz in a granitic melt⁵ was approximately 4.5 moles/kg at $\sim 700^\circ\text{C}$; (2) the interfacial kinetics⁶ was about 10^{-1} cm⁴/mol sec; and (3) the diffusion coefficient of SiO₂ in a silicic melt⁷ ranged from 10^{-5} to 10^{-6} cm²/sec (based on the Stokes-Einstein relation).

The results presented in Fig. 4.9 indicate that r_g increases very nearly as $\sqrt{t}$ with the growth rates being many orders of magnitude greater than those observed for hydrothermal quartz. As the cooling rate is increased from 0.1 K/hr (F), to 0.5 K/hr (G), and finally to 2.5 K/hr (I), the r_g values increase systematically by about one-half order of magnitude. At larger cooling rates (curve I), the growth rate versus time trend bends over for long times. The slight curvature in curve (H) is due to an arbitrary selection of 30 rather than 20 kcal/mol for the Arrhenius slope of solubility. Perhaps most importantly, we see that a change in the diffusion coefficient (curve G, $D = 10^{-5}$ cm²/sec to curve J, $D = 10^{-6}$ cm²/sec) has a marked effect on quartz growth in the melt. Clearly, with such large interfacial kinetics, crystal growth of quartz under the conditions modeled is diffusion-controlled.

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4.2.3 Gas Solubility Experiments: Analysis of Error and Techniques

(S. E. Drummond)

This work will be published as a chapter in a forthcoming book by John Wiley and Sons entitled "Hydrothermal Experimental Techniques." Included in this chapter are discussions of the types and uses of gas solubility data; experimental methods and techniques; errors incurred with each method and ways to minimize them; and data reduction. Two basic methods are generally employed to obtain data on the solubility of gases in high temperature aqueous solutions. The method requiring the least sophisticated equipment, the most labor, and often incurring the greatest errors involves direct sampling of the liquid and/or vapor phases. For most gases, a P-V-T-X method is preferred because sampling and analysis are not required and because more and more accurate data can be taken by this method if the proper techniques are applied and if the conditions of the experiment are controlled to advantage.

There are essentially two categories of the general P-V-T-X method, both requiring that the temperature, pressure, and bulk composition of the system be measured, and that the composition or gas partial pressure be ascertained from the vapor pressure of the system. One technique ($V_V \neq 0$) depends on knowing the volume of the vapor phase either by direct measurement or by partitioning the total volume of the system between the liquid and vapor phases knowing the total mass in the system and the mass densities of each phase. In this case, the composition of the liquid phase is determined from the bulk composition of the system and the composition and volume of the vapor phase. In the other technique, ($V_V = 0$), the volume of the system is changed until the liquid-vapor two-phase boundary near the bubble-point (i.e., system is predominantly liquid) is detected by one of various means.

At this condition, the liquid composition is equal to the bulk composition of the system. Both methods require an independent knowledge of the water vapor pressure in order to determine the partial pressure of the gas from the total pressure just as both methods require a knowledge of the volumetric properties of water vapor and the gas to obtain compositional information on the gas mixture in the vapor phase.

For both types of P-V-T-X experiments, the errors in the measured gas solubilities are greatest for sparingly soluble gases and increase with increasing temperature. For $V_V \neq 0$ experiments, the error can typically be minimized by lowering the gas content of the system. In virtually all cases, a carefully performed P-V-T-X experiment ($V_V \neq 0$ and/or $V_V = 0$ techniques) will produce gas solubility data with an uncertainty of five to ten percent or less.

4.2.4 Formation Constants for Aqueous Ferrous Acetate Complexes at Elevated Temperatures and Pressures from Magnetite Solubility Experiments

(S. E. Drummond, D. A. Palmer)

Our previous results^{1,2} on the kinetics of acetate decarboxylation demonstrated that acetate is sufficiently stable below 300°C to be effective in transporting metals in hydrothermal solutions by enhancing the solubility of minerals through complexation. The overall reaction studied to evaluate metal-acetate formation constants is expressed by the general reaction:

The experiments cover a range from 100°-250°C, 250-1250 bars and CH_3COO^- concentrations from 0.005 to 1.0 m and indicate that the first and second ferrous acetate complexes (i.e., $n = 1$ and 2 for the above reaction) dominate over this entire range of conditions. These data are depicted in Figure 4.10 where, disregarding activity coefficients, a slope of -1 corresponds to the $\text{FeCH}_3\text{COO}^+$ complex and a slope of 0

Fig. 4.10. Dependence of total Fe^{2+} on the concentration of CH_3COO^- . The total iron coordinate is normalized for the acetic acid concentration. Concentration units are molal for CH_3COO^- and CH_3COOH and ppm for ΣFe . Solid lines and symbols are for 1250 bars while dashed lines and open symbols correspond to the 250 bar data. Symbols represent actual data points and the lines represent least-squares regression to a model including the 1,1 and 1,2 ferrous acetate species. At 250°C and 250 bars, the 1,3 species is incorporated in the fit.

corresponds to the $\text{Fe}(\text{CH}_3\text{COO})_2$ complex. Presently, there is little or no evidence for the $\text{Fe}(\text{CH}_3\text{COO})_3^-$ complex; however, due to the well established tendency to form complexes with the highest ligation numbers at the most elevated temperatures, the data currently being taken at 300°C may identify this complex. Figure 4.10 illustrates that the solubility of magnetite varies in a simple and regular manner with changes in temperature, pressure and composition. The agreement between the measured values and the smooth values obtained from a model including the $n = 1$ and 2 species, suggest that the random error in the data rarely exceeds 0.05 log units. Formation constants for the $\text{FeCH}_3\text{COO}^+$ and $\text{Fe}(\text{CH}_3\text{COO})_2$ are plotted in Figure 4.11 and reflect volumes, enthalpies and heat capacities that are all quite sensible for reactions of the general form of the reaction expressed above. After accounting for the redox and hydrolysis equilibria and the solubility of magnetite in the absence of ligand, which are included in this reaction, our solubility data can be used to represent the simple coordination of ferrous and acetate ions in solution:

Fig. 4.11. Temperature and pressure dependence of the formation constants for the 1,1 and 1,2 ferrous acetate species according to the indicated reaction.

In this form, it is convenient to compare the relative strengths of the acetate and chloride complexes. Indeed, such a comparison of these data for the ferrous acetate complexes with the data of Crerar³ for the chloro complexes shows that the formation constant for the $\text{FeCH}_3\text{COO}^+$ species is about 100 times larger than for the FeCl^+ species and that the $\text{Fe}(\text{CH}_3\text{COO})_2$ species is favored by a factor of 10,000 over the FeCl_2 species. Consequently, these data give credibility to the hypothesis that organic complexes are responsible for the mobility of metals in some hydrothermal systems, particularly in sedimentary basins where measured acetate levels reach 0.1 M, and in any setting where a hydrothermal fluid has access to organic material. Clearly, the implications of these data for ore formation, radioactive waste disposal, and corrosion in steam generators, among other geologic and industrial processes, are sufficient to warrant further investigations of organic complexing of metals in hydrothermal solutions.

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3. D. A. Crerar, et al., *Geochim. Cosmochim. Acta* **42**, 1427 (1978).

4.2.5 Direct Comparison of the Formation Constants for Aqueous Ferrous Acetate and Ferrous Chloride Complexes at Elevated Temperatures by Hydrogen-Electrode EMF Techniques

(S. E. Drummond, D. A. Palmer)

The conceptual basis for these experiments originates from the idea that it should be possible to measure in a hydrogen-electrode EMF cell, the relative strengths of the complexes of a metal or cation with any pair of ligands if one of the ligands hydrolyzed appreciably in the pH region of interest. Intro-

duction of the metal ion into a solution containing a hydrolyzing ligand will shift the pH of the solution (and hence the EMF of the cell); due to the coordination of the metal with the basic form of the ligand. The magnitude of the shift depends on the concentration of metal and ligand, the formation constants for the metal-ligand complex, and the concentration of and formation constants for any competing non-hydrolyzing ligand. In the present example where Fe^{2+} is the metal ion, acetate (Ac^-) is the hydrolyzing ligand, and chloride (Cl^-) is the non-hydrolyzing ligand, it can be shown that under conditions where only the 1:1 complexes are significant, the relationship among these variables can be expressed as:

$$Q_{\text{Cl}} = \frac{[\text{FeCl}^+]}{[\text{Fe}^{2+}][\text{Cl}^-]}$$

$$= \frac{(Q_{\text{Ac}} \cdot [\text{Ac}^-]) \cdot ((\Sigma[\text{Fe}]/[\text{FeAc}^+]) - 1) - 1}{[\text{Cl}^-]}$$

where brackets denote concentrations, $Q_{\text{Ac}} = [\text{FeAc}^+]/[\text{Fe}^{2+}][\text{Ac}^-]$, and $\Sigma[\text{Fe}]$ is the total ferrous iron in solution. Of course, this equation is more complicated when multiple complexes of either ligand are involved.

Our preliminary experiments were performed in a hydrogen-electrode concentration cell with a solution of 0.1 M HAc, 0.01 M NaAc and 1.0 M NaCl in both the test and reference compartments which are separated by a liquid junction and share a common vapor. A titrant of 0.25 M FeCl_2 , 1.0 M NaCl, 0.1 M NaAc and 0.01 M NaAc was added stepwise to the test compartment and the EMF shift observed. From previous measurements of ferrous acetate complexes (see 4.2.4), it is possible to know with certainty that the FeAc^+ species was predominant over other acetate complexes, and as a result the concentration of this species can be obtained accurately from the magnitude of the EMF shift. Therefore, $[\text{FeAc}^+]$, Q_{Ac} , $\Sigma[\text{Fe}]$, $\Sigma[\text{Ac}]$, and $\Sigma[\text{Cl}]$ are known, $[\text{Ac}^-] = \Sigma[\text{Ac}] - [\text{FeAc}^+]$, and $[\text{Cl}^-] \approx \Sigma[\text{Cl}]$ (with a very small correction for the amount that is

complexed with Fe^{2+} - a quantity that can be easily solved for by iteration). Consequently, it is possible to get an accurate measure of Q_{Cl} from an independent knowledge of Q_{Ac} and the data from such an experiment. To determine the speciation of the ferrous chloride complexes, it is necessary to collect data over a range of chloride concentrations and reduce the data in a normal fashion by regression analysis. On the basis of our preliminary titration data, the assumption that FeCl^+ is the only ferrous chloride species (necessitated by data from only a single chloride concentration), the formation quotients for FeCl^+ range from about 1.0 to 1.5 log units less than the corresponding values for FeAc^+ from 100° to 300°C. If, as seems likely, other ferrous chloride species (e.g., FeCl_2) are present in appreciable quantities, the relative strength of the FeCl^+ species is even less. This observation is in qualitative agreement with the comparison made in section 4.2.4 between the FeAc^+ and FeCl^+ formation constants. Also, if reasonable values for activity coefficients are assumed for the Fe^{2+} , Cl^- , and FeCl^+ species, the formation constants for FeCl^+ derived from these experiments are between 0.1 (at 100°) and 1.2 (at 300°C) log units larger than given by Crerar.¹ Part of this discrepancy is undoubtedly due to Crerar's handling of activity coefficients. Other possible sources of variance could come from systematic errors in Crerar's data or from our assumption that FeCl_2 is not present in our experiments. Clearly, further experimentation at other chloride concentrations will be required to get unambiguous measures of the ferrous chloride complexes.

These preliminary experiments do show that:

(1) EMF techniques of this kind are capable of producing accurate data for metal complexes; (2) the method is inherently more accurate and much easier than conventional solubility methods; (3) the method could be used to advantage with spectral techniques that could resolve the identity of the species; (4) acetate complexes of iron are indeed much stronger than the analogous chloride complexes; (5) this

method is amenable to measurements in any system wherein the total metal concentration can exceed 10^{-3} M and the difference between the formation constants of the hydrolyzing and non-hydrolyzing ligand do not exceed about 3 orders of magnitude. Lastly, it is easy to see the advantage of having a non-complexing, non-hydrolyzing electrolyte to use as a supporting medium for studies of the complexing of metals with hydrolyzing ligands in the absence of competing ligands. We currently are experimenting with sodium trifluoromethanesulfonate as a non-complexing electrolyte. The results at this juncture are encouraging, and, if successful, will allow this EMF technique to be elevated from a relative to an absolute method for measuring the stability constants of metal complexes.

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4.3 Stable Isotope Geochemistry

4.3.1 Stable Isotope Geochemistry of Tectonic Carbonate Slices in the Brevard Fault Zone, Southern Appalachians

(D. Wesolowski)

This year, the Department of Energy, National Science Foundation, and U. S. Geological Survey began funding research projects under the Continental Scientific Drilling Program (CSDP) which is intended to foster studies that contribute toward a better understanding of the structure and active geologic processes in the continental crust of the United States through direct probing and sampling.

One of the highest priorities for the first ultradeep (>10 km) CSDP drilling project is a site in northwestern South Carolina being investigated by Robert D. Hatcher of the University of South Carolina. Fig. 4.12 summarizes the geology of this region and gives the location of the proposed Appalachian Deep Core Hole (ADCOH).

The unmetamorphosed Valley and Ridge sequence consists predominantly of Cambro-Ordovician continental shelf clastics (sandstones, shales)

Fig. 4.12. Geological map of the ADCOH site region showing the location of carbonate samples discussed in the text. The geologic units are also discussed in the text.

and carbonates (limestones, dolomites).¹ The Blue Ridge and Inner Piedmont Belts are composed of lower Paleozoic high grade metasediments (amphibolite to granulite facies) with eugeosynclinal affinities.¹ These crystalline terrains are separated by the Brevard Fault Zone and the adjacent lower grade (greenschist to amphibolite facies) lower Paleozoic Chauga Belt.¹

Recent deep seismic reflection profiling² suggests that the geologic structure of the

region is as shown in Fig. 4.13, which is a schematic northwest-to-southeast cross section through Fig. 4.12 at the ADCOH site. According to this interpretation, the crystalline metamorphic belts are believed to occur as a thin sheet thrust over remnants of the Valley and Ridge shelf sequence (patterned units in Fig. 4.13) and underlying Grenville-aged basement along a major Alleghenian subhorizontal detachment zone. The Brevard Fault Zone, a prominent physiographic and geologic feature of the Southern Appalachians, is interpreted to be a splay off this major sole thrust. The primary goals of the ADCOH drilling project are to confirm this structural interpretation and to investigate the mechanisms of emplacement of thin crystalline thrust sheets.

As an active member of the ADCOH scientific team, we are conducting geochemical studies of carbonates exposed in the region in order to test the hypotheses presented above and to provide a data base to be used in preparing the formal ADCOH proposal for CSDP funding.

Hatcher³ has mapped a thin, but laterally extensive, carbonate unit along the northwestern margin of the Chauga Belt, referred to here as Chauga River Carbonate (CR in Fig. 4.12). This unit consists of strongly foliated calcite marble containing large amounts of quartz and muscovite. We sampled this lithology at six localities, shown in Fig. 4.12, including one of the shallow holes drilled as part of the ADCOH site survey.

Fig. 4.13. Idealized northwest to southeast cross-section through the ADCOH site.

Within the Brevard Fault Zone, several lenticular bodies of much purer dolomitic marble occur, and Hatcher³ has suggested that these represent tectonic slices of Cambro-Ordovician platform carbonates brought up along the Brevard Fault from beneath the postulated sole thrust during Alleghenian thrusting. Two slices were sampled, a small outcrop at Whetstone near the proposed drill site (W in Fig. 4.12), and an extensive suite of samples from the Fletcher quarry in North Carolina (F in Fig. 4.12).

To provide a data base against which to compare these units, the Valley and Ridge platform carbonates were also studied. Samples of the lower Cambrian Shady Dolomite (S) were collected in the Grandfather Mountain Window and at three sites in the Valley and Ridge. Data on the overlying Conasauga Group carbonates (C) were provided by Steve Haase at ORNL. Kula Misra at the University of Tennessee contributed a suite of samples from the overlying Knox Group (K) in the Copper Ridge District.

Fig. 4.14 summarizes the carbon and oxygen isotopic compositions of 86 samples from these units. The isotopic signature of the Shady and Conasauga samples are within the normal range for unmetamorphosed Cambrian carbonates worldwide. The Knox Group appears to be somewhat depleted in ^{13}C , but is within the normal oxygen range. As can be seen, the Chauga River (indicated by the letter B in Fig. 4.14) and slice carbonates are distinctly anomalous.

Fig. 4.14. Carbon and oxygen isotopic compositions ($\delta^{13}\text{C}_{\text{PDB}}$ and $\delta^{18}\text{O}_{\text{SMOW}}$) of carbonates analyzed in this study.

Mathematical modeling demonstrates that the strong ^{13}C and ^{18}O depletion of the slice and Chauga River carbonates could have resulted from open system exchange with an infiltrating hydrothermal fluid at water-rock mass ratios of around 1-3. Two types of fluids could have produced the observed trends -- $\sim 300^\circ\text{C}$ fluids with initial carbon ($\delta^{13}\text{C}_{\text{PDB}}$) and oxygen ($\delta^{18}\text{O}_{\text{SMOW}}$) isotopic compositions of -10 and 2 permil, respectively; or $\sim 150^\circ\text{C}$ fluids with carbon and oxygen compositions of -10 and -5 permil, respectively. The first type of fluid could have been produced during dewatering of the shelf sequence associated with Alleghenian overthrusting. The second type of fluid could represent a deeply circulating (5-7 km) ground-water of meteoric origin.

There is insufficient supporting evidence to uniquely interpret the isotopic data from the Brevard carbonates at this time. However, we can say with some confidence that hydrothermal alteration of the tectonic slice and Chauga River carbonates has occurred at integrated water-rock ratios of around 1-3. We can also suggest that the carbon isotopic signatures of the slices may be useful for correlation purposes. For instance, the Whetstone slice could represent a tectonic fragment of Shady Dolomite or a member of the Conasauga Group. We have as yet not identified a platform carbonate with a carbon isotopic signature similar to the Fletcher slice. Neither slice appears to have come from the Knox Group.

Additional information needed to interpret these results includes more extensive isotopic analyses of Brevard and platform carbonates coupled with detailed petrography and especially fluid inclusion studies of the altered carbonates to give temperatures of fluid rock interaction and the mole fractions of CO_2 and CH_4 in the fluids. These studies are now underway in collaboration with Robert J. Bodnar at the Virginia Polytechnical Institute.

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4.3.2 Geochemical Evidence for Intense Hydrothermal Alteration of Granitoid Intrusives in the Carolina Slate Belt of North Carolina and Virginia

(D. Wesolowski)

A regional survey of granitoids of the Southern Appalachian Piedmont¹ has revealed a large area of the Slate, Raleigh and Eastern Slate Belts of North Carolina and Virginia in

which the granitoid plutons exhibit anomalously low and highly variable whole-rock $\delta^{18}\text{O}$ values (Figure 4.15). Whole rock oxygen isotopic compositions ($\delta^{18}\text{O}_{\text{WR-SMOW}}$) of 6-8 permil are typical of granitoids derived by partial melting of mantle or lower crustal igneous materials, while granitoids with oxygen isotope compositions greater than 8 permil probably consist partly or completely of melted meta-sedimentary material.² As can be seen in Figure 4.15, many of the granitoids in the study area have $\delta^{18}\text{O}$ values less than 6 permil,

Fig. 4.15. Whole rock oxygen isotopic compositions ($\delta^{18}\text{O}_{\text{WR-SMOW}}$) of granitoid plutons of the Slate, Raleigh, Eastern Slate and "?" Belts of the Piedmont of Southern Virginia and northern North Carolina. Stippled pattern indicates the base and precious metal mineralized zones of the Virginia District along the Virginia-North Carolina border and the Gold Hill District further south. Asterisks indicate pyrophyllite mines and prospects in the area. Plutons: HP = Highpoint, PC = Farks Crossroads, RX = Roxboro, VC = Vance County, BV = Burkeville, RO = Rolesville, PB = Petersburg, F = Fountain.

with several in the range -1 to 3 permil. These very low and highly variable oxygen isotope signatures are indicative of extensive exchange of the intrusions with isotopically depleted (in ^{18}O versus ^{16}O) waters of either meteoric or regional metamorphic origin.²

The available data on the oxygen isotopic compositions of mineral separates from all Southern Appalachian intrusions^{1,3} support the premise of isotopic re-equilibration at temperatures substantially below the crystallization temperatures of the melts, as shown in Table 4.1. Granitoids with high quartz oxygen isotopic compositions show small positive quartz-alkali feldspar fractionations indicative of primary fractionations frozen in during crystallization and cooling of the intrusives, including the Petersburg granite in the study area (PB in Fig. 4.15). However, the strongly depleted granitoids of the study area exhibit large positive quartz-alkali feldspar fraction-

ations indicating exchange at much lower temperatures (400 to less than 200°C) with an ^{18}O -depleted fluid.

The low grade (lower greenschist facies) metasedimentary country rocks of the main Slate Belt (Fig. 4.15) are predominantly acid to intermediate volcanics and lava flows believed to represent an early Cambrian island arc sequence.⁴ The country rocks of the Eastern Slate Belt are apparently similar in age and origin.⁵ Much of the Raleigh Belt is believed to consist of a Grenville-aged (1 billion year old) continental-metasedimentary terrain.⁵ Little is known about the country rocks in the area east of the Raleigh Belt designated the "?" Belt in Fig. 4.15.

The granitoids of the main Slate Belt, including the Highpoint (HP), Parks Crossroads (PC), Roxboro (RX), Vance County (VC) and Burkeville (BV) plutons in Fig. 4.15, are lower Cambrian in age and exhibit shallow, subvol-

Table 4.1

Oxygen Isotope Data Available from
Southern Appalachian Granitoids

	$\delta^{18}\text{O}_q (\text{‰})^A$	$\delta^{18}\text{O}_q - \delta^{18}\text{O}_{\text{af}} (\text{‰})^B$	$T(^{\circ}\text{C})^C$
Data from twenty plutons in Georgia, South and North Carolina ³	7-12	1.0 - 1.5	400-600
This Study:			
Rockford	10, 13	0.9, 0.9	500-600
Gunpowder	8.5	0.5	700-800
Ellicott City	avg. 9.8	avg. 1.4	400-500
Petersburg (PB) ^D	7.5	0.7	500-600
Rolesville (RO) ^D	5.4	1.9	300-400
Highpoint (HP) ^D	5.1	2.4	200-300
Fountain (F) ^D	4-7	avg. 3.6	<200

^AOxygen isotopic composition of quartz from the granitoid.

^BDifference in oxygen isotopic composition between quartz and alkali feldspar.

^CApproximate temperature at which this difference would represent an equilibrium fractionation.

^DGranitoids shown in Fig. 4.15.

canic characteristics. Thus, the depleted oxygen isotopic signatures of these intrusions could be explained as having resulted from the shallow (1-2 km) circulation of heated, isotopically depleted meteoric waters so common in such settings throughout geologic time.² The occurrence of numerous "volcanic exhalative" base and precious metal deposits in this region⁶ (stippled areas in Fig. 4.15) are evidence of intense hydrothermal circulation in the volcanic country rocks surrounding the granitoids. Pyrophyllite deposits ($\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$), which are very common in the Slate Belt (asterisks in Fig. 4.15), are also considered to be metamorphosed equivalents of intense silicic hydrothermal alteration zones found in many active continental volcanic settings.⁴

Feiss⁴ postulated extensive regional hydrothermal alteration of the Slate Belt volcanics, based on major element trends. The depleted oxygen isotope values of the associated granitoids in this area offer the first direct evidence that large-scale meteoric-hydrothermal circulation systems were active in the Slate Belt.

The gravity map compiled by Haworth⁷ shows that the area of numerous strongly depleted Cambrian granitoids in the Slate Belt coincides with a very prominent gravity high, indicating dense material in the lower crust of this region. We interpret this to represent a large mafic batholith which was the source of volcanic and intrusive activity and the heat engine driving regional meteoric hydrothermal convection. This interpretation implies that the Slate Belt was not decoupled from its lower crust during Alleghenian thrusting.

The Raleigh and Eastern Slate Belts both contain strongly depleted granitoids which are believed to be Alleghenian in age (~200 million years ago), including the Rolesville (R0) and Fountain (F) plutons in Fig. 4.15. However, they intrude metavolcanics which are reported to be Precambrian to Cambrian in age (~600 million years ago).

If these intrusives were subvolcanic and associated with meteoric hydrothermal altera-

tion, then one might expect some coeval Alleghenian sediments or volcanics in the area. No sedimentary or volcanic rocks of this age have been reported from either the Raleigh or Eastern Slate Belt.

Another possibility is that the Alleghenian intrusives assimilated isotopically depleted slate belt volcanics during intrusion. Farrar⁵ has suggested that the contact between the Raleigh and Slate Belt lithologies is a regional pre-Alleghenian detachment zone separating Grenville-aged continental/metasedimentary crust from overthrustured Slate Belt volcanics. However, Sans⁸ found extreme local variability in the whole-rock oxygen data from the Fountain Pluton in the Eastern Slate Belt. This is more typical of hydrothermal alteration than assimilation.

Obviously more detailed work is needed to sort out the geologic relationships in this region. More detailed studies are now being conducted in collaboration with Geoffrey Feiss at the University of North Carolina to test some of the hypotheses put forward above. We have collected over 100 samples of "unaltered" Slate Belt volcanics as well as pyrophyllitic "altered" volcanics from the area immediately west and south of the Parks Crossroads pluton in the Slate Belt of North Carolina. Major and trace element measurements of these rocks are now being conducted with ORNL support at the University of North Carolina, and whole rock oxygen isotope measurements will be completed at ORNL within the next few months. These results will help establish whether meteoric or regional metamorphic fluids accomplished the isotopic alteration of plutons like the Parks Crossroads intrusion. Similar detailed studies are planned for the depleted granites and their country rocks in the Raleigh and Eastern Slate Belts.

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4.3.3 Modeling of Stable Isotopic Exchange Between Minerals and Fluids During Simultaneous Diffusion and Chemical Reaction

(D. R. Cole)

Oxygen isotopic exchange between minerals and fluids has been attributed to two major processes, diffusion and dissolution-precipitation (interfacial phenomena).¹ At the one extreme, when minerals and fluids are in chemical equilibrium, oxygen isotopic exchange occurs primarily through a diffusion mechanism. On the other hand, isotopic exchange in mineral-fluid systems that are initially far from chemical equilibrium may be controlled largely by surface reactions.¹ Heretofore, isotopic exchange in natural systems has been modeled for conditions where only one mechanism was thought to prevail, i.e., only diffusion or only surface reactions. It is clear that most geologic systems involve fluid-mineral interaction where both processes are occurring simultaneously, and thus the question that we need to address is -- what are the rates of isotopic equilibration for systems affected by both processes?

In order to solve this question, we need to quantify the rate of uptake of the oxygen-bearing species (e.g., H_2O) by the solid phase (e.g., mineral) through which it can diffuse and with which it can also react chemically. This can be regarded as a problem in diffusion in which some of the diffusing substance becomes immobilized as diffusion proceeds, or as

a problem in chemical kinetics in which the rate of reaction depends on the rate of supply of one of the reactants by diffusion. Initially, we chose to model oxygen isotopic exchange between K-feldspar and a 0.1 M NaCl solution where the surface reaction mechanism is first-order and reversible. The behavior to be expected when the reaction is reversible depends on the relative rates of diffusion and reaction. When the reaction is very rapid, we can assume that the immobilized component (new phase) is always in equilibrium with the component free to diffuse, and diffusion is the rate-controlling process. At the other extreme is the case of diffusion being so rapid compared to reaction that the concentrations of diffusing substance and immobilized product are effectively uniform throughout the medium and the isotopic exchange is controlled solely by the reversible reaction. For isotopic exchange accompanying simple cation-exchange reactions (e.g., $K/\text{feldspar} + NaCl \rightleftharpoons Albite + KCl$), the former case of rapid reaction-slow diffusion is most appropriate.¹ The other case appropriate for natural systems, where rapid irreversible chemical reactions take place, will not be considered here.

Let us consider a sphere of uniform composition of radius a that is placed in a solution and that the solute is allowed to diffuse into the sphere. As diffusion proceeds, a first-order, reversible isotopic exchange reaction occurs and a product, which is non-diffusing, is formed. The concentration of solute in the solution is always uniform (C_0), while initially the sphere is free from solute. Let C be the concentration of ^{18}O -bearing solute free to diffuse within the sphere and S that of the ^{18}O -immobilized solute, each being expressed as amount per volume of sphere. Diffusion in the sphere then follows

$$\frac{\partial D}{\partial t} = D \left(\frac{\partial^2 C}{\partial x^2} - \frac{2}{x} \frac{\partial C}{\partial x} \right) - \frac{\partial S}{\partial t}$$

and we assume the simultaneous reaction to be of the form

$$\frac{\partial S}{\partial t} = r_f C - r_b S$$

where D is the diffusion coefficient and r_f and r_b are the rate constants of the forward and reverse reactions, respectively. Thus the immobilized solute (new phase) is formed at a rate proportional to the concentration of solute free to diffuse, and disappears at a rate proportional to its own concentration. We require solutions of these two expressions with the initial conditions of $S = C = 0$, $x < a$, $t = 0$ and with a boundary condition expressing the fact that the rate at which solute leaves the solution is equal to that at which it enters the sphere over the surfaces, $x = \pm a$. We also need to account for the case where the ^{18}O -concentration just within the sphere is K' times that in solution, where K' is the equilibrium isotope partition ratio between solid and solution corrected for concentration.¹ Given these considerations, we can express the fractional approach to isotopic equilibrium (F) for a sphere, modified from Crank,² as

$$F = 1 - \sum_{n=1}^{\infty} \frac{(1+\beta)\exp(p_n t)}{1 + \left[1 + \frac{r_f r_b}{(p_n + r_b)^2} \right] \left[\frac{2\pi a^3}{V} - \frac{p_n}{20k_n^2} + \frac{V p_n^2}{8\pi a D^2 k_n^2} \right]}$$

where the p_n 's and k_n 's are given by

$$\frac{V}{4\pi D a} (p_n) - 1 = -k_n a \cot(k_n a),$$

$$k_n^2 = -\frac{p_n}{D} \frac{p_n + r_f + r_b}{p_n + r_b}$$

and

$$\beta = \frac{3V}{4\pi a^3 (K' + 1)}, \quad M_{\infty} = \frac{VC_0}{1 + \beta}$$

where V is the volume of solution.

We used the expression for (F) to model oxygen isotopic exchange between K-feldspar and a 0.1 m NaCl solution for a β (corrected

water/rock ratio) of >10 (fluid in a large fracture interacting with feldspar in the host rock). The diffusion coefficient data for K-feldspar are taken from Gilotti and others,³ and the surface reaction isotopic rates are from Cole.⁴ The curves given in Fig. 4.16 are for the following conditions (at 1 kbar):

- A: $T=650^\circ\text{C}$, $a=0.022$ cm, $K'\sim 10$, $r_f a^2/D \sim 0.1$
- B: $T=500^\circ\text{C}$, $a=0.022$ cm, $K'\sim 5$, $r_f a^2/D \sim 1.0$
- C: $T=350^\circ\text{C}$, $a=0.022$ cm, $K'\sim 2$, $r_f a^2/D \sim 10$
- D: $T=650^\circ\text{C}$, $a=0.007$ cm, $K'\sim 10$, $r_f a^2/D \sim 0.01$
- E: $T=650^\circ\text{C}$, $a=0.07$ cm, $K'\sim 10$, $r_f a^2/D \sim 1$
- F: $T=650^\circ\text{C}$, $a=0.22$ cm, $K'\sim 10$, $r_f a^2/D \sim 10$

The most interesting result to come from these calculations is that the effect of the very rapid isotopic exchange accompanying surface reaction (nearly instantaneous) is to slow down the diffusion process. The overall diffusion process with reaction is slower than the simple diffusion process by a factor of about $(K' +$

Fig. 4.16. Fraction of oxygen isotopic exchange (F) plotted versus time in years for coupled surface reaction and diffusion in the system K-feldspar + 0.1 m NaCl. See the text for the conditions used to model curves A-F.

1). Thus, for the condition used to give curve A, an equilibration time of approximately 3000 years is obtained compared to only about 250 years for simple diffusion. As anticipated, an increase in the time required for isotopic equilibration corresponds to a decrease in the temperature of interaction (curves A, B, C). The magnitude of this change is a function of the change in K' (which decreases with decreasing temperature) and r_p^2/D , the modified rate constant (which increases with decreasing temperature). Finally, we observe that as grain size increases, so does the time required for isotopic equilibration (curves A, D, E and

F). This effect appears to become more pronounced for a grain radius in excess of about 0.05 cm for the conditions modeled at 650°C.

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5. MATERIALS CHEMISTRY

The activities of the first part of this program (Sections 5.1.1 - 5.1.10) are focused on (1) the exploitation of nonequilibrium surface-modification techniques for the development of a better understanding of catalytic processes, and (2) the development of new methods for the synthesis of advanced (nonoxidic) ceramic materials. Research in the area of heterogeneous catalysis involves the application of ion implantation, ion-beam mixing, and related nonequilibrium processing methods to the generation and systematic investigation of well-defined catalytically active surfaces (e.g., electrocatalysis of Cl_2 and O_2 evolution reactions at Ru-implanted titanium electrodes). Rutherford backscattering, photoacoustic and photocurrent spectroscopies, and electrochemical techniques are used to determine the kinetics and mechanistics of the catalyzed reaction, the properties of the catalyst, and the specific mode of operation of the catalyst. Chemical research in the area of advanced ceramics is directed toward the development of generalized methodologies for the preparation of nonoxidic ceramic materials (BN, Si_3N_4 , SiC, and the borides, nitrides, carbides, and carbonitrides of the transition metals of groups 4, 5 and 6). Inorganic and organometallic precursor compounds are synthesized by low temperature methods (e.g., in liquid NH_3), and subsequently pyrolyzed or photolyzed to yield ceramic powders, fibers, or films. High temperature reactions are also being investigated, and are illustrated by the reactions of SiS with NH_3 to form $\alpha\text{-Si}_3\text{N}_4$ and BPO_4 with molten NaCN to form BN. Techniques applied to the characterization of intermediate and final products synthesized in the ceramic program include UV-Vis-FTIR and Raman spectroscopies, x-ray diffraction, and thermal analysis (DTA/TGA-mass spectroscopy). The second part of this program (Sections 5.2.1 - 5.2.6) is concerned with the structure and dynamics of several materials. The purpose of this program is to understand and predict bulk mechanical, transport, thermodynamic, and other physical properties from a characterization at the molecular level. Sections 5.2.1, 5.2.4, and 5.2.5 discuss work on the structure of polymeric and amorphous materials. Section 5.2.2 discusses a study of diffusion in polystyrene. Section 5.2.6 presents some results on intramolecular motion. This treatment is based on classical and semiclassical mechanics. Section 5.2.3 discusses a technique for centering a sample in a diffractometer and for aligning the diffractometer.

5.1 Chemistry of Advanced Inorganic Materials

5.1.1 Surface Engineering of Mixed Oxide Layers with Electrocatalytic Properties

(C. E. Vallet, C. W. White,¹ J. L. Moore¹)

Electrocatalysis processes are catalyzed surface processes taking place at the electrolyte/electrode interface. Ion implantation, which allows controllable modification of the near surface region (typically less than 100 nm), has been recently used in catalysis studies.^{2,3,4} Results show promise for designing new catalysts and for testing fundamental mechanisms occurring at modified electrodes.⁵

In a first modification scheme, ruthenium was implanted into titanium at different doses. Then, a mixed-oxide layer ($\text{RuO}_2\text{-TiO}_2$) was formed electrochemically in order to produce models for the "dimensionally stable anode" used in the

industrial production of chlorine from NaCl.⁶ Figure 5.1 shows typical ^{102}Ru concentration profiles in titanium measured by Rutherford backscattering after implantation of various doses ranging from 1×10^{16} atom cm^{-2} to 1×10^{17} atom cm^{-2} . Because only low intensity ruthenium beams were obtainable, the implant times were relatively long, e.g., 7 hours for a dose of 5×10^{16} atom cm^{-2} . As is well-known, the implantation of low doses generates concentration profiles close to gaussian; therefore, few implanted atoms are present at the surface. This can be a drawback for implantation in its use for producing a catalytic surface if there is no way to dissolve the substrate surface. Since titanium was expected to dissolve during the electrochemical treatment, the implantation procedure was designed to obtain a near constant concentration over a

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Fig. 5.1. Ruthenium concentration profiles after implantation into titanium at three energies (40, 70 and 130 keV). The various total doses are indicated.

significant part of the profile. Thus, electrochemical measurements could be carried out on an electrode surface with a constant and well-defined composition while cutting through the profile. This goal was achieved by successive implantations at different energies. The implanted profile, concentration C at depth x , can be calculated,^{7,8} at each energy by

$$C(x) = \frac{\phi}{(2\pi)^{1/2} n \Delta R_p} \exp\left[-(x-R_p)^2 / 2(\Delta R_p)^2\right] \quad (1)$$

where ϕ is the fluence in atom cm^{-2} , n the atomic density, R_p the projected range and ΔR_p the longitudinal straggling (or range spread). Figure 5.2 shows the predicted profile for a total dose of 2.4×10^{16} atom cm^{-2} with 20% of the total dose introduced at the lowest energy of 40 keV, 27% at 70 keV, and 53% at 130 keV. The predicted profile gives a 30 nm layer with a Ru/Ti ratio on the order of 0.1. The predictions compare quite well with the measured profile on the sample with a total dose of 2.5×10^{16} atom cm^{-2} implanted according to this scheme and shown in Figure 5.1. As the dose increases, the sputter erosion of the surface

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Fig. 5.2. Predicted ruthenium concentration profile produced by multienergy implantation into titanium.

during implantation moves the maximum concentration towards the surface and ultimately leads to a steady-state limit where the previously implanted atoms are removed as fast as new atoms are introduced. The sputtering effect can be observed in Figure 5.1, where the maximum concentration is shifted towards the surface as the dose increases. For the highest fluence (1×10^{17} atom cm^{-2}), the concentration at the surface is nearly the maximum concentration, indicating that the sputtering limit is almost reached. These results indicate that no composition higher than 30-35% in ruthenium will be achieved by ion implantation of ruthenium in titanium.

An alternative approach is to use the ion-beam mixing technique.⁹ In a first attempt, a thin layer of ruthenium having a thickness of 20 nm (determined by backscattering) was electrolytically deposited on a titanium surface using an Engelhard sulfamate bath at 75°C. Mixing was attempted with a 300 keV xenon beam and a dose of 2×10^{16} atom cm^{-2} . The mixing was not clearly demonstrated by backscattering. Sputtering of the surface may have occurred, and future attempts will be made at lower Xe doses on possibly thinner plated layers.

Figure 5.3 shows the potentiodynamic polarization curves obtained in 1 M (HCl + NaCl, pH = 1) for a titanium electrode, a ruthenium-plated electrode, and a ruthenium implanted electrode containing about 28% ruthenium atoms at its surface. The ruthenium oxide layer was deposited by evaporating $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ and firing at 500°C under an oxygen flow.¹⁰ The resulting surface was a dark blue porous powder for which the effective area was much larger than the geometric one. All the electrodes containing ruthenium exhibited a sharp increase in current around 1.05V/SCE, corresponding to chlorine evolution. Currents obtained at the ruthenium implanted electrode, with the low ruthenium content of 28%, are only ten times less than those obtained at the ruthenium-plated electrode or at the RuO_2 -coated electrode of larger effective area.

Fig. 5.3. Potentiodynamic polarization curves in 1M(HCl + NaCl, pH = 1) at 25°C: Titanium; — RuO_2 coated titanium; — ruthenium plated titanium and ruthenium implanted titanium. The scan rates are indicated along the polarization curves.

These first results demonstrate the possibility of producing by ion implantation well-defined electrodes with catalytic activity similar to that of usual mixed-oxide electrodes.

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5.1.2 Electrocatalysis of Cl_2 and O_2 Evolution Reactions at Ru-Implanted Titanium Electrodes (E. J. Kelly, D. E. Heatherly)

The intent of the present research is to demonstrate the value of nonequilibrium surface-modification techniques (ion-beam implantation, ion-beam mixing, etc.) for the generation and study of catalytically active surface materials. For this purpose, electrocatalysis of Cl_2 evolution by a mixed-oxide catalyst ($\text{RuO}_2 + \text{TiO}_2$) on a titanium substrate was investigated. The "dimensionally stable anode" (DSA) currently used in the chlor-alkali industry for the electrocatalytic production of Cl_2 consists of a conducting mixed-oxide catalyst layer, RuO_2 (~30-40 mol%)- TiO_2 , on a tita-

nium substrate. The catalyst is formed on the substrate by thermal decomposition of an alcoholic solution of RuCl_3 or $\text{RuCl}_3 + \text{TiCl}_4$ (or $\text{Ti}(\text{OR})_4$) at 300–500°C in air. Due to the variability of the surface area (up to 250 times the projected area), composition, and structure, a fundamental understanding of the catalytic process has remained elusive.¹ In the present work, these problems have been largely overcome by using ion-beam implantation to prepare the catalyst. Near-surface Ru-Ti alloys were generated by implanting Ru into zone-refined titanium, and characterized (Ru concentration vs distance from surface) by Rutherford backscattering.² For a sample implanted with 1×10^{17} atom Ru cm^{-2} , the Ru concentration in the alloy is virtually constant (28 atom % Ru) to a depth of approximately 20 nm, and then decreases to essentially zero over the next 100 nm (see Section 5.1.1 for details). For lower Ru implant doses, the Ru concentration rises to a maximum and then decreases to zero with increasing depth. A sample doped at 1×10^{16} atom Ru cm^{-2} , for example, exhibits a maximum concentration of 3 atom % Ru at a depth of 20 nm, with the concentration decreasing to virtually zero at the surface. In the potential region of interest for Cl_2 and O_2 evolution, the surface of the alloy is anodically oxidized to form the mixed-oxide ($\text{RuO}_2 + \text{TiO}_2$) catalyst layer (<~3.0 nm thick).

In Fig. 5.4, potentiodynamic polarization curves are shown for titanium in 1 M ($\text{HCl} + \text{NaCl}$, pH = 1.0), and for Ru-implanted titanium in 1 M ($\text{HCl} + \text{NaCl}$, pH = 1.0) and in 0.5 M ($\text{H}_2\text{SO}_4 + \text{Na}_2\text{SO}_4$, pH = 1.0). The initial potential of 0.9 V vs SCE is too negative for Cl_2 and O_2 evolution to occur, and only small background currents associated with the oxidation of substrate metal are observed. As the potential is increased into the region where Cl_2 and O_2 evolution become thermodynamically possible, the curve for titanium shows no evidence of either gas being evolved. This observation is consistent with the fact that, in the potential region of interest, the metal is

Fig. 5.4. Potentiodynamic polarization curves: (Δ) = Ru-implanted (1×10^{17} atom cm^{-2}) titanium in 1M($\text{HCl} + \text{NaCl}$, pH = 1.0) and in 0.5M($\text{H}_2\text{SO}_4 + \text{Na}_2\text{SO}_4$, pH = 1.0), respectively; ($\bullet$) = titanium in 1M($\text{HCl} + \text{NaCl}$, pH = 1.0). Electrode area (projected) = 0.31 cm^2 , scan rate = 0.1 mV s^{-1} , He atmosphere, $T = 30.0^\circ\text{C}$. Currents normalized to 0 curve at 0.9 V vs SCE.

covered with a thin protective layer (~3 nm) of n-TiO_2 , a poorly conducting semiconductor known to be incapable of supporting significant anodic (oxidation) currents.³ In contrast to pure titanium, the curve for Ru-implanted titanium in chloride-free sulfate solution shows a large (~100 fold) rise in the current corresponding to the oxygen evolution reaction. Similar results were obtained in 1 M ($\text{HClO}_4 + \text{NaClO}_4$, pH=1.0). The observed Tafel slope, $d \ln i / dE$, of $3F/2RT$ is characteristic of the O_2 evolution reaction.⁴ In the chloride solution, there is observed a very large rise in the current at the Ru-implanted electrode due to Cl_2 evolution. Although the standard potential for the Cl_2 evolution reaction (1.12 V vs SCE) is more positive than that for the O_2 evolution reaction (0.99 V vs SCE), evolution of Cl_2 occurs at a lower potential than evolution of O_2 because of the greater overvoltage for the

latter reaction.¹ The current observed in the 1 M $[\text{Cl}^-]$ solution is due almost entirely to Cl_2 evolution.

As shown in Fig. 5.4, the Cl_2 evolution reaction is also characterized by a Tafel slope of 40 mV/decade, i.e., $(\partial \ln i / \partial E) = 3F/2RT$. This result is indicative of a reaction sequence in which a 1-electron transfer reaction is in virtual equilibrium, with the product of the reaction serving as a reactant in a subsequent rate-determining 1-electron transfer reaction. It has frequently been suggested that the mechanism of chlorine evolution is given by reactions 1 and 2,

where the subscript "a" refers to the adsorbed state.¹ The current density (i) corresponding to this mechanism is given by Eq. 3,

$$i/F = 2(k_2 k_1 / k_{-1}) [\text{Cl}^-]^2 \exp(3FE/2RT) \quad (3)$$

where E is the electrode potential, $k_{\pm j}$ are chemical rate constants for the j^{th} reactions, and the other symbols have their conventional significance. According to Eq. 3, the reaction order (n) with respect to the chloride ion concentration, i.e., $(\partial \log i / \partial \log [\text{Cl}^-])_E$, must equal 2. In Fig. 5.5, the effect of Cl^- concentration on the Cl_2 evolution reaction is shown for Ru-implanted Ti at 1.10 V vs SCE. One observes that with increasing $[\text{Cl}^-]$, the order decreases from 2 and approaches a limit of 1. This result cannot be explained by the mechanism given by reactions 1 and 2. However, all of the observed results are compatible with the mechanism,

Fig. 5.5. Effect of chloride ion concentration on the rate (current) of Cl_2 evolution at a Ru-implanted (1×10^{17} atom cm^{-2}) titanium electrode in $1\text{M}(\text{HClO}_4 + \text{NaClO}_4, \text{pH} = 1.0)$ at 1.10 V vs SCE.

where the indicated reactions occur only at surface Ru sites. For this mechanism, the current density expression consistent with the observed Tafel slope and reaction order is given by Eq. 7,

$$i/F = 2S(k_6 k_5 [\text{Cl}^-] / k_{-5}) \left(\frac{k_4 [\text{Cl}^-]}{k_4 [\text{Cl}^-] + k_{-4}} \right) \times \exp(3FE/2RT) \quad (7)$$

where S represents the Ru sites cm^{-2} at the electrode surface. As evidenced by a loss of catalytic activity, and confirmed by Rutherford backscattering, Ru-implanted electrodes held at a potential in the Cl_2 evolution region for a period of several weeks lose all implanted Ru. If the slow dissolution of the electrode is nonselective, S should exhibit a maximum value corresponding to maximum Ru concentration in the original implant profile. It has been observed that the maximum current (at constant E and $[\text{Cl}^-]$) is indeed proportional to the maximum concentration of Ru in the profile which, in turn, is proportional to the total implant dose. Finally, it should be noted that the high current densities and the magnitude of the observed Tafel slopes are not compatible

with a semiconducting oxide layer. The loss of semiconducting properties which accompanies the implantation of Ti with Ru has been confirmed by photoacoustic spectroscopy and photocurrent measurements (see Section 5.1.3).

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5.1.3 Photoacoustic and Photocurrent Spectroscopy of Ruthenium-Implanted Titanium Electrodes in HCl Solution, Preliminary Results (C. E. Vallet, J. S. Hendrickson¹)

In situ photoacoustic and photocurrent spectroscopies have been used earlier² to monitor semiconducting oxide film growth at titanium electrodes during passivation in 1 M H₂SO₄ solution. Titanium dioxide (anatase) layers as thin as 2 nm were detected by an increase in the photoacoustic signal at a wavelength corresponding to the semiconductor band-gap energy, as well as by the simultaneous appearance of a photocurrent. Photocurrents, corrected for light intensity, were found to be roughly proportional to the thickness of the layer. Recently, these two spectroscopies have been applied to the in situ characterization of

the surface of ruthenium-implanted titanium electrodes in 1M(HCl + NaCl, pH = 1) solution at the onset of chlorine evolution (i.e., 0.9 V/SCE) and in the Tafel region (i.e., 1.1 V/SCE).^{3,4} For reference, spectra also have been measured on a titanium electrode and on a RuO₂-coated electrode, for which the potentiodynamic polarization curves are shown in Section 5.1.1.

Figure 5.6 shows the in-phase photoacoustic spectrum of the titanium electrode maintained at 1.1 V/SCE, with a background current of about 0.06 μ A, and the photocurrent spectra generated during the recording of the two in quadrature components of the photoacoustic signal. The three spectra agree with the assumption of an anatase layer at the surface.²

Similar measurements were made on the ruthenium-implanted titanium electrode (1×10^{17} atom cm⁻²) in order to elucidate the nature of the interface which exhibits electrocatalytic activity even for a low ruthenium content.⁴ The spectra obtained at 0.9 V/SCE and at 1.1 V/SCE are shown in Figs. 5.7 and 5.8 respectively. The electrode was placed in 1M(HCl + NaCl, pH = 1) solution and maintained

Fig. 5.6. In-phase photoacoustic spectrum (—) at a titanium electrode in 1M(HCl + NaCl, pH = 1) solution and associated photocurrent spectra (...) and (---) recorded during measurement of the in quadrature components of the photoacoustic signal.

Fig. 5.7. Time dependence of photoacoustic spectra (—) and photocurrent spectra (...) at a Ru-implanted titanium electrode (1×10^{17} atom cm^{-2}) in $1\text{M}(\text{HCl} + \text{NaCl})$, $\text{pH} = 1$ solution. #1, 6 hours after immersion; #2, 1 day; #3, 5 days, and #4, 7 days after immersion.

Fig. 5.8. In-phase photoacoustic spectra (—) and simultaneous current variations (...). Current variations (---) observed for the electrode in the dark over a time period similar to that spent for recording one photoacoustic component spectrum.

at 0.9 V/SCE. After six hours, the current appeared fairly stable ($0.1 \mu\text{A}$), and spectrum 1 was taken. Subsequent spectra (2,3,4) were obtained one, five, and seven days later,

respectively. Between the spectroscopic measurements, potential scans up to 1.1 V/SCE showed excellent reproducibility for the values of the current as well as for the slope (40 mV/decade). A typical scan is shown in Section 5.1.1. The photoacoustic and photocurrent spectra have the general features of those obtained on the titanium electrode and indicate the presence of anatase on the electrode surface. Although no changes with time are observable by photoacoustic spectroscopy, the associated photocurrent nearly doubles in a period of five days. Ultimately, a constant value for the maximum of photocurrent is reached, as indicated by the identity of spectra 3 and 4. The observed photocurrents are about 10 times smaller than those measured at a titanium electrode. This difference cannot be attributed solely to the lower titanium content (70%), and suggests that implanted ruthenium atoms may modify the energy levels in the titanium dioxide, i.e., increase the probability for hole-electron recombination. In order to test this hypothesis, future experiments are planned for electrodes implanted with various doses, and for an anodically grown anatase layer which has been implanted with ruthenium.

Measurements on the same electrode polarized at 1.1 V/SCE with a background current on the order of $3\text{--}4 \mu\text{A}$ were made at a lower light-chopping frequency in order to obtain a larger photoacoustic signal ($\sim \omega^{-1}$) for extraction from the erratic noise produced by chlorine evolution at the electrode. The photoacoustic spectrum, in Fig. 5.8, does not show any change in slope around 400 nm, indicating no or very little semiconducting TiO_2 at the surface. Moreover, the variations in current observed during various photoacoustic measurements do not show any correlation with wavelength; instead, they are similar to those observed in the dark over similar time periods as shown in Fig. 5.8. As chlorine evolution takes place at the ruthenium-implanted titanium electrode, both spectroscopies agree with a surface layer for which the anatase like semiconducting properties have been lost. The photoacoustic and

photocurrent spectra of a RuO₂-coated titanium electrode are also "featureless," i.e., they are similar to those shown in Fig. 5.8 rather than those shown in Figs. 5.6 or 5.7. Indeed, ruthenium dioxide is known to be a metallic conductor.

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5.1.4 Synthesis of BN Using BPO₄ as the Boron Source

(C. E. Bamberger and G. M. Begun)

Hexagonal BN has many industrial applications in which high temperature stability or high electrical resistance are required. Among the many synthetic methods known for the preparation of BN powders, some employ the strong reducing conditions provided at high temperatures by NaCN to reduce and nitride B₂O₃, but part of this boron is converted to sodium bicrates. In seeking alternative reactions that would convert all the boron to BN, we studied the reaction of NaCN with BPO₄. The experiments consisted of heating intimately ground mixtures of BPO₄ and NaCN, in various proportions, under flowing Ar or N₂ to several temperatures up to 1020°C. The weight losses were recorded and the reaction products were analyzed by Raman spectroscopy and x-ray diffraction (XRD) before and after removal of water soluble species. Raman spectroscopy was also used to identify the sodium phosphates present in aqueous solution. It was found that the critical parameters were: temperature, length of time, and the ratio NaCN/BPO₄. The reactions were relatively slow at temperatures below 1000°C; about 17 h at this temperature were required for completion of the reaction.

Ratios of NaCN/BPO₄ = 2 to 4 yielded black products containing graphitized carbon; ratios smaller than 2 yielded white to gray products and, therefore, were thoroughly studied.

The identification of the species and the quantitative weight-loss data obtained by heating, and by water extraction, enabled us to describe the reactions as a function of NaCN/BPO₄ by the following equations:

for $1 < x < 1.455$

for $1.455 < x < 1.714$

for $1.714 < x < 2$

The hexagonal BN synthesized by the reactions represented by Eqs. 1-3 was identified by XRD; Raman spectroscopy could not be used due to the high fluorescence of the samples. The latter is very likely caused by the presence of trace amounts of carbon since it has been proven elsewhere that carbon is the source of high fluorescence in BN. Scanning electron microscopy (SEM) examination of the BN powders revealed that they consist of irregularly shaped particles of 1 micrometer or less on their longest axis. All the reactions studied can be used either as a method for producing BN or as a means of disposing of NaCN while converting it into a marketable product. The inherent high fluorescence of the BN powders

obtained by means of the reactions studied may be applied to tribology studies in which the presence of minute amounts of fluorescent BN can be ascertained by means of an exciting light.

5.1.5 Reaction of Silica with NaCN at 1000°C (C. E. Bamberger)

There is no information available on the interaction of silica with molten or gaseous alkali cyanides except that it results in degradation of the silica. The behavior of alkali cyanides at high temperatures has been studied, but the reported results are not in satisfactory agreement. Thus, the reaction of SiO_2 with NaCN is being studied because it may be conducive to the synthesis of either SiC or Si_3N_4 , both advanced refractory materials of considerable industrial interest, and because a thorough understanding of that reaction may indirectly provide information on the thermal decomposition of alkali cyanides. The experiments consist of heating up to 1000°C mixtures of silicic acid ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$) with NaCN, under flowing N_2 , in BN or graphite containers.

Examination by x-ray diffraction of the obtained products revealed the absence of crystalline phases. However, after annealing the products for 3 to 5 days at 800°C, the presence of $\alpha\text{-Na}_2\text{Si}_2\text{O}_5$ was demonstrable. After treatment of the annealed products with hot water and aqueous HF, the residues still contained substantial amounts of silicon as indicated by energy dispersive x-ray analysis (EDX). Exploratory qualitative tests of ammonia evolution (reaction of the annealed products with molten KOH) were positive, suggesting that only a small amount of Si_3N_4 or $\text{Si}_3\text{C}_3\text{N}$ may be present. This leads to the speculation that the bulk of the silicon present in the HF-extracted residues occurs as amorphous SiC. Work is continuing in attempts to confirm this and to identify the source of N_2 .

5.1.6 Raman Spectral Study of Ion Implantation Effects in SiC

(G. M. Begun, C. J. McHargue,¹ J. M. Williams²)

Ion implantation and ion-beam mixing are being increasingly used to alter the near-surface region of materials other than semiconductors. Recently, there has been renewed interest in the study of the structure and properties of ceramics subjected to such treatments. Because of the non-equilibrium nature of such treatments and the complex nature of ceramic structures, progress in understanding the damaged microstructures has lagged behind that for metals and alloys. Laser Raman spectroscopy is proving useful in observing changes in the surface layers of solid ceramics. Our Raman spectra were observed by focusing the light from an argon-ion laser (514.5 nm) on the surface of a SiC crystal at 45° to the normal and observing the Raman spectrum at 90° to the exciting light.

Figure 5.9 shows the Raman spectra of an unimplanted $\alpha\text{-SiC}$ crystal and of similar crystals implanted with nitrogen (62 keV) to fluences of 2.7×10^{15} , 2.7×10^{16} , and 1.6×10^{17} atom cm^{-2} , corresponding to 0.54, 5.4, and 32 dpa units, respectively. Displacements per atom (dpa) is a calculated unit of fluence or dose used in order to compare the effects from implanting ions of different masses and energies. The two strong peaks at 784 and 959 cm^{-1} are the transverse optical (TO) and longitudinal optical (LO) vibrations of the SiC crystal lattice. The auxiliary peaks at 150, 768, and 796 cm^{-1} are characteristic of the 6H $\alpha\text{-SiC}$ polytype structure. The rising background of several of the Raman spectra is due to traces of fluorescence from impurities accumulated during the implantation process.

As SiC becomes disordered the sharp peaks broaden until they vanish in amorphous samples. In amorphous materials, all vibrational modes can contribute to the first-order Raman scat-

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Fig. 5.9. Raman spectra from α -SiC implanted with nitrogen (62 keV) to 0.54, 5.4, and 32 dpa at 300 K, 514.5 nm excitation.

tering, which results in a spectrum with broad peaks related to the density of states as determined by neutron scattering. In the case of SiC, the completely amorphous material shows very few spectral features.

With increasing nitrogen fluence, the peaks in the Raman spectra became weaker until all disappeared after 32 dpa irradiations,

indicating complete amorphization of the sample. The Rutherford backscattering spectra (RBS), on the other hand, indicated that disorder of the SiC surface was attained at a lower fluence. It is not clear whether the slow disappearance of the Raman spectral peaks with increasing fluence, as compared to the RBS data, was due to a spreading depth of amorphization or to an increasing opacity of the surface layer of SiC.

Wright and co-workers^{3,4} showed broadened and weakened Raman peaks for the crystal vibrations of α -SiC amorphized by H^+ , D^+ , and He^+ ion implantations. There is no evidence in the spectra of Fig. 5.9 for the C-C or Si-Si bonds reported by Gorman and Solin⁵ for sputter deposited amorphous SiC films. Thus, decomposition of the SiC by the bombarding ions is not indicated. Broad bands centered at 1360 and 1585 cm^{-1} (C-C bonds) or near 480 cm^{-1} (Si-Si bonds) are reported for non-stoichiometric samples of SiC.⁶

The Raman spectra for a virgin crystal of α -SiC and for one after implantation to 2.2 dpa with 2×10^{15} Cr atom cm^{-2} (260 keV) are shown in Fig. 5.10. The spectrum of the implanted sample contains no detectable peaks. The amorphous (disordered) state as defined by Rutherford backscattering was reached at a fluence of 0.25 dpa. The Raman peaks disappeared in the chromium-implanted samples at much lower fluences than for nitrogen-implanted samples, indicating a more rapid increase in the amorphization or the opacity of the surface layer. Raman spectral techniques thus add additional original and supplemental data to that obtained by other methods of examining ion-implanted materials.

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Fig. 5.10. Raman spectra from α -SiC implanted with chromium (280 keV) to 2.2 dpa at 300 K, 514.5 nm excitation.

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5.1.7 Thermal Decomposition of Organometallic Compounds of Titanium and Vanadium (Gilbert M. Brown)

The refractory carbides, nitrides, and borides of groups 4, 5, and 6 of the periodic table, in addition to being heat resistant, are extremely hard and have high thermal and electrical conductivities. These materials are generally prepared by direct combination of the elements at high temperature.¹ The products are generally powders and must necessarily be sintered, compressed, or extruded to yield a useful high-density physical form. The advantages gained by pyrolysis of a precursor compound, already in the desired physical form, have been exploited in the preparation of SiC from polycarbosilanes and in the formation of metal-oxide ceramic materials via sol-gel processing.² A general route to the preparation of the previously mentioned refractory materials via the precursor concept is a worthwhile goal. The controlled thermal decomposition of

organometallic compounds is extensively utilized in the electronic industry for the chemical vapor deposition of metals and semiconductors of the group 12-16 elements.³ Decomposition of organometallic compounds of groups 4 and 5 containing a boron, nitrogen, or carbon moiety may be a viable route to borides, nitrides, or carbides of these elements. Furthermore, these precursor compounds contain an organic group to which a polymerization site can be readily attached. In this way, organometallic polymers may be formed which can be decomposed to refractory fibers or sheets in analogy to the formation of SiC fibers from polycarbosilane fibers. The decomposition of bimetallic compounds may be a route to ternary refractory materials with highly controlled stoichiometry.

There are precedents in the literature for the formation of refractory materials from the pyrolysis of metal-organic compounds of groups 4 and 5. The compounds, $(C_5H_5)_2Ti(L)_2$, where L is CH_3 , C_6H_5 , or Cl , decompose to TiC in a H_2 atmosphere above 900°C.⁴ The CVD of a film consisting of a carbonitride of titanium was produced at <600°C from tris(2,2'-bipyridine) titanium.⁵ The dialkylamides of titanium, zirconium, vanadium, niobium, and tantalum have been shown to be promising precursors to metal nitrides and carbonitrides.^{6,7} The metal nitrides form on thermal decomposition in the temperature range of 300-500°C. The kinetics and products of the pyrolysis of tetrakis-(diethylamide)titanium have been studied in some detail.⁷ A polymer of the composition $-[Ti(NC_2H_5)]_n-$ was suggested as an intermediate in the formation of TiC_xN_{1-x} . In general, the mean bond dissociation energies of metal-carbon bonds for metal-carbonyl, metal-alkyl, and π bonded metal arene compounds of groups 4 and 5 are less than the corresponding metal-anionic ligand bond energies.⁸ Therefore, the compound $Ti(C_5H_5)(N(CH_3)_2)_3$ might be expected to decompose to TiN rather than TiC.

The temperature-programmed thermal decomposition (TPTD) of some representative titanium and vanadium compounds has been investigated. The TPTD apparatus consisted of a furnace in

which the temperature could be increased linearly with time (5-10° per min) from ambient to ~700°C. The furnace was swept with a stream of He or Ar to carry the gaseous products to a thermal conductivity gas detector. The compounds, $(C_5H_5)_2ML_2$, where M is Ti or V and L is an anionic ligand including CN, NCS, or NCO, were prepared by reacting $(C_5H_5)_2MCl_2$ with the appropriate alkali metal salt. The gas evolution vs temperature profiles for the compounds were remarkably similar. As the temperature was increased to a threshold value, the evolution of gas increased rapidly to a maximum and then decreased at higher temperatures. The profiles were reasonably symmetrical about the maxima, with a half-maximum width of around 15 to 20°C. At higher temperatures, secondary gas evolution processes occur, but they are drawn out over a larger temperature range (100°C). The compound, $V(C_5H_5)_2(CN)_2$, has its first gas evolution maximum at 265°C and a secondary peak in the range 450-500°C. The characteristics of the signal from the thermal conductivity detector suggest the secondary evolution is primarily hydrogen. The compounds, $V(C_5H_5)_2(NCS)_2$ and $Ti(C_5H_5)_2(NCS)_2$, had first gas evolution maxima at 320°C and 275°C, respectively.

The thermal decomposition of $V(C_5H_5)_2(CN)_2$ was studied in more detail than the other compounds. Weight loss for reaction in an He or Ar stream at 350°C corresponds to the loss of one cyclopentadiene ring. The infrared spectrum of the 350°C pyrolysis product shows loss of both the C-N stretching vibration and the C-H stretching vibration. Pyrolysis to 275°C does not cause complete loss of the C-H and C-N vibrations. The CN stretch changes from a sharp doublet (2108 cm^{-1} and 2115 cm^{-1}) in the starting compound to a broad series of 5 peaks from 2210 cm^{-1} to 2080 cm^{-1} . In the C-H stretching region, the 275°C product has a peak at 3110 cm^{-1} , appropriate for an aromatic hydrocarbon and also observed in the starting compound, and a new peak at 2939 cm^{-1} , appropriate for an aliphatic hydrocarbon. Carbon analysis for the 350°C pyrolysis product corresponds to the formula $VC_{2.3}$; apparently

one C_5H_5 ring is lost and the second decomposes or fragments to carbon and hydrogen. X-ray diffraction of the product of decomposition of $(C_5H_5)_2V(CN)_2$ at 500°C (in a sealed tube under vacuum) indicates the product is completely amorphous. The decomposition of the compounds, $M(C_5H_5)_2(NCS)_2$, where $M = (Ti, V)$, were plagued by loss of some material from the furnace by transpiration in the He stream, but the weight loss on heating corresponds to loss of at least one cyclopentadiene ring. The infrared spectrum for the product of $Ti(C_5H_5)_2(NCS)_2$ pyrolysis at 350°C shows loss of the C-N stretching vibration and the C-H stretching vibration. These results are encouraging since the ligands surrounding these metal ions are lost at the relatively low temperature of 350°C, but it is surprising that a hydrocarbon is apparently fragmented at this temperature. The TPTD apparatus is being upgraded to incorporate a Hewlett-Packard Model 5970 mass selective detector in place of the thermal conductivity detector for analysis of the evolved gases. In situ analysis of the solids will be attempted by FTIR spectroscopy using a controlled atmosphere heated stage reflectance attachment.

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5.1.8 Surface Photochemical Reactions of Ceramic Precursors

(Gilbert M. Brown, L. Maya)

A new program was initiated to study the photochemical formation of refractory materials (such as the carbides, nitrides, borides, silicides, etc. of groups 4, 5, and 6 of the periodic table) by either direct photolysis or through a photochemically promoted heterogeneous reaction between an organometallic film and a reactive gas phase. In general, some parallel between the thermal and photochemical decomposition reactions of precursor molecules can be expected, and we will compare and contrast the mechanistic pathways for product formation by the two methods.

There is interest in the deposition of ceramic materials in general and particularly in temperature sensitive materials such as organic polymers or semiconductors. The electronic industry is interested in "laser direct writing"¹ of metals and ceramic materials for applications such as high density microcircuits. In this method, highly focused laser sources can be used to generate features on a surface in the size range 0.2-1.0 μm . In addition to deposition of a material on a surface, laser processes include surface etching and surface alloying. For the deposition of materials, several approaches have been reported. These include the absorption of photons in a gas layer adjacent to the substrate, absorption of photons by a surface adsorbed phase, and absorption by the substrate itself. Ultraviolet or visible light in general promotes photochemical reactions resulting from electronic excitation, whereas infrared lasers promote thermal decomposition via vibrational excitation. We will concentrate on the electronic excitation photochemistry of adsorbed

molecules. These will be unimolecular reactions (or bimolecular reactions involving a second nonabsorbing reactant in the gas phase) using chemically specific visible or low energy ultraviolet light.

An apparatus to allow the transmission UV-Vis spectrum and IR spectrum of an adsorbed layer on a substrate as well as UV-Vis photolysis was designed and constructed. The compound of interest is sublimed onto the substrate which is placed in a rotatable holder within an enclosed cell maintained under vacuum or filled with a reactive gas. The cell is provided with windows for transmission of both IR and UV-Vis photons. The substrate can be oriented parallel to salt windows for IR spectroscopy or, by a 90° turn, oriented parallel to quartz windows for UV-vis spectroscopy and photolysis.

In an experimental test of the apparatus, TiBr_4 was sublimed onto a KBr plate. The titanium compound was rendered nonvolatile by reacting it with ammonia vapor. The IR spectrum showed a superposition of bands characteristic of the expected Ti(IV) ammonolysis product, $\text{Ti}(\text{Br})(\text{NH}_2)_3 \cdot 2\text{NH}_3$,² and NH_4Br . Photolysis with a 1000 W Xenon arc lamp converted the pale yellow film to a dark deposit. Infrared spectroscopy showed only the spectrum of NH_4Br ; the Ti(IV) ammonolysis product had been presumably converted to TiN.

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5.1.9 Study of Gaseous and Solid Silicon Monosulfide as Precursors for Silicon Nitride and Silicon Carbide

(J. Brynestad, J. F. Land)

In attempts to find new routes for the preparation of silicon nitride and silicon carbide powders, we have been studying the

reactions of silicon monosulfide with ammonia gas and various hydrocarbons. Preliminary studies revealed that gaseous silicon monosulfide reacted completely with ammonia gas at 1100°C to form a white amorphous powder with submicron particle size distribution and containing 17.3 weight % sulfur.¹ Forsyth² reported a process for producing ultrafine silicon nitride by reacting silicon monosulfide with ammonia gas at ~1400°C. He synthesized silicon monosulfide by adding iron monosulfide or iron disulfide to molten ferrosilicon. He claimed that silicon nitride is formed if the reaction products are exposed to temperatures in the range 1250°C to 1500°C before cooling. He did not report that the reaction products contained sulfur.

We have studied the reaction of gaseous silicon monosulfide with ammonia in more detail. Pure silicon monosulfide is easily synthesized by reacting hydrogen sulfide with excess elemental silicon or ferrosilicon alloys in a vertical reactor at temperatures > 1090°C (i.e. the melting point of silicon disulfide). The reaction scheme is

The reaction between ammonia and gaseous silicon monosulfide was studied in the temperature range 1100-1400°C. The gases were mixed in a reaction chamber and subsequently rapidly cooled. The reaction products were white and amorphous. They all contained various amounts of sulfur, in the range 17-27 weight %. Products with the lower sulfur contents were obtained when the ammonia was used in large excess. It also was found that at temperatures higher than ~1400°C the reaction does not go to completion, even with a large excess of ammonia, as evidenced by contamination of the end product with unreacted silicon monosulfide. This result can be attributed to the decomposition of ammonia into nitrogen and hydrogen before entering the reaction zone. This is in agreement with previous observations, that a mixture of nitrogen and hydro-

gen does not react readily with silicon monosulfide gas.¹

The sulfur present in the uncontaminated powder is not easily removed. Treatment at 1000°C with ammonia gas did not reduce the sulfur content. Even heating at 1400°C in flowing ammonia gas for 24 hours did not remove all the sulfur. However, heat treatment in ammonia gas (or a nitrogen/hydrogen mixture) at temperatures higher than ~1450°C removed the sulfur completely and converted the amorphous powder into α -silicon nitride. The aforementioned results are not in agreement with the observations reported by Forsyth.

Solid silicon monosulfide was observed to react with ammonia gas at temperatures as low as 50°C, forming a white powder. However, it was observed that the reactivity of different batches of the solid silicon monosulfide varied greatly, depending upon its history. It appears that rapidly quenched silicon monosulfide yields the most reactive product. The white reaction products invariably contained sulfur in the range 23-42 weight %. Heating the reaction products at 1000°C in flowing ammonia did not reduce the sulfur content below 27 weight %. Heating to 1500°C in ammonia (or nitrogen/hydrogen mixtures) converted the powder to sulfur-free α -silicon nitride.

Preliminary experiments have shown that silicon monosulfide reacts with ethylene at as low a temperature as 200°C. Again, the reactivity of the solid monosulfide varied widely from batch to batch, the most rapidly quenched silicon monosulfide being the most reactive. Attempts to convert the black reaction products into crystalline silicon carbide by heating gave confusing results; whereas heating the reaction products to 1000°C in argon did not give any weight change, further heating of the product to 1500°C (in argon) resulted in complete volatilization of the samples. This phenomenon will be studied further.

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5.1.10 Precursors of Titanium Carbonitrides (L. Maya)

A series of novel compounds was isolated in the course of exploratory work on the chemistry of titanium halides in liquid ammonia. This work was undertaken to identify synthetic approaches to titanium-containing precursors of ceramic materials. Representative of these compounds is a mixed valence Ti(III)-Ti(IV) amido bridged tetramer, $[\text{NH}_4^+ \cdot \text{NH}_3]_2[\text{Ti}_4\text{Br}_4(\text{NH}_2)_{12}]^{-2}$, which was produced by the reaction of potassium borohydride and titanium (IV) bromide in liquid ammonia at room temperature. Similar ammonium salts of either Ti(IV) or Ti(III) were also prepared. A representative listing of some of these compounds, including the analyses and mode of preparation, is given in Table 5.1. The reac-

tion of the ammonium salts with sodium acetylide in liquid ammonia evolves acetylene in an amount equivalent to the ammonium ion present. This provided the charge of the complex and yielded novel titanium acetylide derivatives. The acetylides convert into titanium carbonitrides upon thermal treatment to 800°C. The results of a number of experiments involving the pyrolysis of some of the acetylides are summarized in Table 5.2.

The reaction of titanium halides or their ammonolytic products with sodium acetylide in liquid ammonia to yield halogen-free acetylide precursors having a relatively high titanium content appears to be a convenient synthetic approach. This is made possible by the fact that the alkali metal halide by-products are soluble and easily separated in that reaction medium. This approach appears to be a generalized route applicable to a number of transition metal elements of interest.

Table 5.1 Ammonolytic products of titanium halides and selected derivatives

Compound	Idealized Formula	Calc. wt %					Found wt %						Remarks
		Ti	NH ₃	Br or Cl	K or Na	C	Ti	NH ₃	Br or Cl	K or Na	B	C	
I	$(\text{NH}_4^+ \cdot \text{NH}_3)_2\text{Ti}_4\text{Br}_4(\text{NH}_2)_{12}$	24.78	35.17	41.34			26.1	33.9	40.6	.2	.4		From TiBr_4 and KBH_4 at 25°C. Ti III 13.37% or 51.2% of ΣTi
I'	$(\text{NH}_4^+ \cdot \text{NH}_3)_2\text{Ti}_4\text{Br}_4(\text{NH}_2)_{12}$	24.78	35.17	41.34			24.7	34.8	40.6	.2	.5		From TiBr_4 and KBH_4 at 25°C. Ti III 13.15% or 53.4% of ΣTi
Ia	$\text{KTi}_4(\text{NH}_2)_{12}\text{Br}_3$	28.92	30.79	36.19	5.90		29.1	31.0	36.4	7.1			From I and KNH_2 at -50°C
Ie	$\text{Ti}_4(\text{C}\equiv\text{CH})(\text{NH})_8\text{NH}_2$	59.39	36.88			7.44	58.5	35.0	0.1	2.6		7.6	From I and $\text{NaC}\equiv\text{CH}$
II	$[\text{NH}_4^+]_4\text{Ti}_4\text{Cl}_8(\text{NH}_2)_8 \cdot 4\text{NH}_3$	25.78	36.60	38.16			25.6	36.9	36.9	0.5	0.7		From $\text{TiCl}_3 + \text{NaBH}_4$ at 35°C. Ti III 25.81% or 100% of ΣTi
IIa	$\text{Ti}_4(\text{C}\equiv\text{C})_2(\text{NH})_4$	63.95	22.70			16.02	59.4	20.6	2.8	5.0		12.7	From II and $\text{NaC}\equiv\text{CH}$ at 25°C
III	$[\text{NH}_4^+]_2\text{Ti}_4\text{Br}_4(\text{NH})_4(\text{NH}_2)_6$	27.47	29.25	45.84			27.5	30.9	41.6				Ammonolysis of TiBr_4 after removal of NH_4Br
IIIa	$\text{Ti}_4(\text{C}\equiv\text{C})(\text{NH})_7$	59.76	37.11			7.49	58.7	32.8		5.3		6.9	From III and $\text{NaC}\equiv\text{CH}$

Table 5.2 Pyrolysis of Acetylides

Compound	Idealized Formula	Wt loss to 800°C (%)	Formula of Residue	C Content		Calc wt loss (%)	Remarks
				Calc	Found		
IIb	$\text{NaTi}_4(\text{C}\equiv\text{C})_2(\text{NH})_4\text{NH}_2$	23.9	$\text{Ti}_4\text{N}_2\text{C}_2$	9.85	9.16	28.1	(a) Sodium mirror analyzed, accounts for 65% of initial Na (b) X-ray shows $\text{Ti}(\text{N},\text{C})$
IIc	$\text{Na}_4\text{Ti}_4(\text{C}\equiv\text{C})_2(\text{NH})_2$	21.3	$\text{Na}_4\text{Ti}_4\text{C}_2$	7.8	8.54	21.5	Mostly amorphous shows weak lines of $\text{Ti}(\text{N},\text{C})$
IIIa	$\text{Ti}_4(\text{C}\equiv\text{C})(\text{NH})_7$	24.0	$\text{Ti}_4\text{N}_3\text{C}$	4.88	3.1	23.4	X-ray shows $\text{Ti}(\text{N},\text{C})$ Raman shows $\text{Ti}(\text{N},\text{C})$
IIIB	$\text{NaTi}_4(\text{C}\equiv\text{C})(\text{NH})_7\text{NH}_2$	32.0	$\text{Ti}_4\text{N}_3\text{C}$	4.88	4.66	31.7	X-ray shows $\text{Ti}(\text{N},\text{C})$ Sodium mirror produced

5.2 Structure and Dynamics of Advanced Polymeric Materials

5.2.1 Structure in SiS

(B. K. Annis, J. Brynstad, G. M. Begun)

It is generally thought that solid SiS in the so-called "yellow" form is amorphous, but beyond that, very little is known about the compound on an atomic scale. A neutron diffraction study was carried out at the High Flux Isotope Reactor, and the results yield a radial distribution function (RDF) which represents a weighted summation of all the pair interactions S-S, S-Si, and Si-Si. The principal feature of the RDF is a well-defined peak corresponding to an average nearest neighbor interatomic spacing of 2.15 ± 0.05 Å. The gaseous phase of SiS has been well characterized, and the molecule is known to have a bond distance of 1.93 Å. The width of the peak in the RDF for the solid is sufficiently narrow such that little, if any, SiS can exist with an unchanged bond length.

Since both amorphous and crystalline silicon have a bond length of 2.35 Å, and sulfur-sulfur bonds are typically in the range 2.06 - 2.18 Å, we cannot a priori discount the possibility

that all of the interactions contribute to the first coordination shell. In this case, the area under the RDF peak can be related to the coordination numbers by

$$0.742 (\pm 0.08) = 0.173 N_{\text{SiSi}} + 0.236 N_{\text{SiS}} + 0.0816 N_{\text{SS}}, \quad (1)$$

where the constant on the left was obtained by numerical integration of the RDF between 1.85 and 2.55 Å; N_{ij} refers to the average number of j atoms in this range about any i atom. The total number, N , of nearest neighbors in this range of distances about an i atom is then $N_{ij} + N_{ii} = N$. The numerical coefficients of the N_{ij} are functions of the atomic fractions and the neutron scattering lengths. One equation involving three unknowns would appear to be of little value, but, in fact, we are able to eliminate some possibilities for the coordination numbers.

For example, since low temperature melts of sulfur are thought to consist of chains and rings of double coordinated atoms, since divalent Si compounds are well known, and since Si_2S_2 dimers have been observed, we can postu-

late that SiS is composed of chains such that each atom has two nearest neighbors. Such a chain may be realized in a variety of ways: first, the atoms could be randomly distributed along the chain; this would result in the set $N_{SiSi} = N_{SS} = N_{SiS} = 1$; second, diatomic SiS units randomly connected require $N_{SiS} = 1.5$ and $N_{SiSi} = N_{SS} = 0.5$; finally, SiS units connected in the form SiS - SiS - SiS require $N_{SiS} = 2$ and $N_{SS} = N_{SiSi} = 0$. It can be readily seen that these models will not satisfy Eq. 1. Similarly a model based on a tetrahedral network with atoms or diatomic SiS units randomly distributed on the net leads to $N_{SiS} = N_{SiSi} = N_{SS} = 2$ or $N_{SiSi} = N_{SS} = 1.5$ and $N_{SiS} = 2.5$ respectively. Here again, neither set of N_{ij} will satisfy Eq. 1. Consequently, the diffraction measurements eliminate some of the models that have been successfully applied to melts and other amorphous materials.

At this point, it appears that a model involving dangling bonds or an average over different types of coordination sites is probable. For example, SiS₂ glass is thought to consist of chains of edge shared tetrahedrons such that $N_{SiS} = 4$ and $N_{SiSi} = 2$. In order to preserve the stoichiometry of SiS, it could be postulated that the remaining Si is in the form of amorphous silicon or as micro-crystallites with $N_{SiSi} = 4$. When the appropriate averages are taken, $\bar{N}_{SiS} = 2$, $\bar{N}_{SiSi} = 2$, $N_{SS} = 0$, and Eq. 1 is satisfied to within experimental error. Raman scattering results lend some credence to this picture since the data show some features which could be attributed to clusters of Si distributed amongst chains of tetrahedral SiS₂. However, it may well be that this is not a unique interpretation of the data, and more detailed modeling is in progress.

5.2.2 Small-Angle Neutron Scattering Study of Self-Diffusion in Polystyrene

(B. K. Annis, G. D. Wignall,¹ S. Berr²)

There are at least two broad areas of polymer science for which a knowledge of diffusion is important. On the one hand, polymer diffusion coefficients are necessary for the under-

standing and characterization of polymer interfaces and composite systems which are of current technological concern; on the other hand, theories of polymer behavior at the molecular level can make predictions which require accurate experimental data for comparison. In regard to the latter aspect, the dependence upon molecular weight and temperature are of principal interest. A technique for measuring self-diffusion coefficients for polymer melts using small angle neutron scattering (SANS) has been recently reported in the literature, and it was felt that the method could be usefully applied to a study of self-diffusion in polystyrene.

The SANS method requires a sample in the form of a laminate of alternating deuterated and protonated polystyrene. It is essential that degree of polymerization of the two species be closely matched and highly monodisperse. The appropriate raw materials were obtained from Polymer Laboratories for molecular weights of 117,000, 200,000 and 517,000. Attempts to solvent cast films proved to be futile, and hot pressing was used instead. Typically the resulting laminates were composed of 15 to 20 pairs of 30 micron thick films. Films in the 10 to 15 micron range would be desirable in order to reduce the time for sufficient mixing of the two species to occur. However, practical limitations led to the use of the thicker films. The hot press method was also attempted for films for molecular weight 80,000, but these were found to be too brittle to be useful. The laminates were held between quartz plates and annealed for various times in an argon atmosphere at 235°C. This temperature was chosen to facilitate comparison with some existing data for lower molecular weights which were obtained using an NMR technique. The SANS measurements were made at room temperature after annealing. Despite substantial efforts to outgas the polymers before and after the film preparation, bubble formation of varying extents was noticeable during the annealing stages. Attempts were made to empirically correct for the bubbles, but the origin and possible effect upon the diffusion process is

unknown. A theoretical model developed by de Gennes³ predicts that the diffusion coefficients vary as the inverse square of the molecular weight. Our results gave an inverse power dependence of 1.7 with an experimental uncertainty that would include the theoretical result. When the results of the NMR work⁴ were extrapolated to the molecular weight range of our data, the former were found to be higher by a factor of 2 to 3. This confirms a similar difference between NMR and SANS work by others on self-diffusion in polyethylene and suggests that the molecular motions measured by NMR are not purely diffusive. Another comparison is possible with the Doi-Edwards theory⁵ which provides a possibility of estimating the product of the self-diffusion coefficient and the square of the molecular weight. This may be used to obtain a value of $0.22 \text{ cm}^2/\text{sec}$, whereas the SANS results yield $0.35 \pm .08$ (the NMR work gave $1.0 \text{ cm}^2/\text{sec}$).

Other self-diffusion coefficients for polystyrene have been found in the literature and are scattered over the molecular weight range 2×10^3 to 2×10^6 g/mole and a temperature range of 150–235°C. Most of this data including our SANS work can be brought into qualitative agreement assuming an Arrhenius form of temperature dependence and an empirically determined activation energy of 75 kJ/mol. It appears that our results are qualitatively correct but have limited quantitative value. Furthermore, our experience indicates that development of a reliable technique for generating a wide variety of well-behaved polymer films would require a substantial amount of further investigation which would detract from our other programmatic interests.

5.2.3 Least-Squares Determination of Instrument Errors for X-ray and Neutron Diffractometers

(W. R. Busing)

The four-circle diffractometer is a versatile instrument for the study of crystals or oriented materials by x-ray or neutron scattering. A necessary initial step for any data collection is the determination of parameters which define the crystal lattice and sample orientation. Preliminary parameter values can be calculated from observations of the diffractometer angles required to center three reflections in the counter, and precise values can be determined by a least-squares refinement based on many such measurements. Methods for making these calculations have been developed and described in detail by Busing and Levy.^{1,2}

The early work assumed the sample crystal to be correctly centered on a perfect diffractometer well aligned with respect to the primary beam. But in modern experiments with samples mounted in cryostats or furnaces, it is not always easy to center the sample visually. Moreover, when the entire instrument must be moved in and out of the beam at neutron or synchrotron sources, or when the beam is obtained from adjustable monochromators, it is desirable to have a simple experimental way of checking the alignment. Other workers^{3,4} have described ways of calculating the centering errors and beam-direction errors from the angles observed for a reflection using eight different settings of the diffractometer, but some of these settings require moving the counter through the primary beam, a procedure which is usually inconvenient. This report describes a way of including these error parameters in a general orientation least-squares calculation. The procedure has been included in program ORDIF written to control diffractometers at the HFIR and at conventional x-ray and synchrotron sources. Although the diffractometer axes can usually be adjusted to be parallel or perpendicular to each other using optical or mechanical measurements,⁵ the deviations from perfect adjustment have also been included as optional parameters in this refinement program.

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Maximizing the intensity of a reflection and centering it in the counter produces three independent observations. These are the instrument angle which establishes the Bragg condition and two other angles which center the reflection horizontally and vertically. If the only purpose of the refinement is to determine the unit cell precisely, it may be desirable to use only Bragg angles as observations. It is also possible to use as observations the peak positions obtained from the intensity scans of a standard data collection.

The least-squares parameter list includes the wavelength, six crystal lattice parameters, eight angles (five of them redundant) which define the sample orientation, three angle-dial zero corrections, three sample centering errors, and three parameters which define the source and counter displacements. In addition to these 24 quantities, an option is provided to include three translational errors and three orientational errors for each of the four axes, making a total of 48 parameters.

It is the task of the least-squares program to use the trial values of these 48 parameters, together with the reflection indices and certain instrument angles which serve as independent variables, to calculate an angle to be compared with its observed value. The matrix mathematics involved in making this calculation will be described elsewhere.⁶ Numerical differentiation is used to compute the contribution of each observation to the matrix and vector of the normal equations. Solution of these equations yields the desired parameter changes. Because the problem is nonlinear, several cycles are required for convergence.

Lattice parameters may be constrained to conform to crystal symmetry, and the user is allowed complete freedom in the selection of variables. Care must be taken in this selection, however, to avoid redundancies and poorly determined combinations of parameters. For example, it is not possible to vary the wavelength and all the cell edges together. In the refinement of instrument errors, the size of the data set and the choice of the reflections

included has some effect on which parameters can be determined.

In order to facilitate the selection of variables and to diagnose problems when they occur, the program can be made to perform principal component analysis. In this procedure the eigenvalues and eigenvectors of the matrix of normal equations are obtained. One or more zero eigenvalues will be found if the matrix is singular, and small eigenvalues indicate a poorly conditioned matrix. The corresponding eigenvectors are the coefficients of the linear combination of parameters which cannot be determined. Thus if two parameters are exactly redundant, a zero eigenvalue will result, and the corresponding eigenvector will have only two nonzero elements, the coefficients of these two parameters. Use of the principal component analysis procedure makes it easy for the user to obtain the reliable least-squares results needed to center the sample, align the instrument, and thus to insure the collection of precise intensity data.

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5.2.4 Lattice Models for Polymeric Systems (E. Johnson)

The Flory-Huggins method¹ is probably the most successful theoretical method for obtaining thermodynamic properties of polymer systems. It has been established that relatively simple modifications of the Flory-Huggins method can greatly increase the accuracy of

results and the range of applications.² This article describes a general technique for modifying the Flory-Huggins approach such that accuracy and range of applicability increase.

The Flory-Huggins method is based on the concept of lattice fluids. The distinguishing feature of lattice fluids is that the positions of particles of the system are sites on a lattice. The lattice fluid approach does not contain any inherent limitations on the kinds of systems treated, since the properties of a lattice fluid approach the properties of a "real" fluid as the distances between lattice sites approach zero.^{3,4}

The approach for improving the treatment of lattice fluids under consideration here is based on a set of exact equations for particle distribution functions. There are three equations involved. The third equation of the set was derived for classical systems which have a pairwise additive potential energy function. The other two equations are valid for all classical statistical mechanical systems. The first equation is the two-particle Ornstein-Zernike equation.^{5,6} The second is the integrated Baxter equation.^{7,8} The third is a variational equation.^{9,10}

These three equations form a closed and exact set of equations for the two and three particle distribution functions. For a one component system, the two and three particle distribution functions are denoted by $g^{(2)}$ and $g^{(3)}$, respectively. The particle number density is denoted by ρ . It is equal to the number of particles in a system divided by the volume of the system. The quantity $\rho^2 g^{(2)}(r_1, r_2)$ is the probability density for finding one particle at position r_1 and for finding a different particle at position r_2 . The quantity $\rho^3 g^{(3)}(r_1, r_2, r_3)$ is the probability density for finding three different particles at positions r_1, r_2 , and r_3 . The set of three exact equations is sometimes difficult to solve accurately, because the third equation is ill-conditioned. Ill-conditioned equations are often difficult to solve accurately on a computer because of computer round-off error.

The effect of computer round-off error on solutions to the set of three equations is illustrated here by solutions obtained using different levels of numerical precision in the computer calculations. The results are for the two-dimensional nearest neighbor interaction lattice gas. The results in Table 5.3 are for $u/k_B T = -0.7$ and $\rho = 0.01$ where u is the value of the nearest neighbor interaction energy, k_B is the Boltzmann constant, T is the absolute temperature, and ρ is the particle number density. For the lattice gas, the particle number density is equal to the number of particles in the system divided by the number of lattice sites in the system. In the tables, (x, y) are the cartesian coordinates of the difference of the position vectors of two particles. In the calculations to obtain the results in Column I of Table 5.3, the lowest numerical precision used was REAL*4 or about 7 significant figures. For Column II, the lowest numerical precision used was REAL*8 or about 16 significant figures. If it is assumed that the REAL*8 results are more accurate than the REAL*4 results, then the results in Column I are accurate to four significant figures.

The results in Table 5.4 are for $u/k_B T = -2$ and $\rho = 0.01$. For the results in Columns I and II, the lowest numerical precisions used were REAL*4 and REAL*8, respectively. If it is assumed that the REAL*8 results are more accurate than the REAL*4 results, then the results in Column I of Table 5.4 are accurate to one significant figure. The results in Tables 5.3

Table 5.3

$g^{(2)}(x, y)$ for the two-dimensional nearest neighbor interaction lattice gas. $u/k_B T = -0.7$ and $\rho = 0.01$. Column I: REAL*4. Column II: REAL*8.

x	y	I	II
0	0	-0.0001	-0.0001
1	0	1.9744	1.9743
1	1	1.0193	1.0192

Table 5.4

$g^{(2)}(x, y)$ for the two-dimensional nearest neighbor interaction lattice gas. $u/k_B T = -2$ and $\rho = 0.01$. Column I: REAL*4. Column II: REAL*8.

x	y	I	II
0	0	-0.046	-0.047
1	0	6.863	6.654
1	1	1.796	1.668

and 5.4 show that as the temperature decreases, the effect of computer round-off error increases.

The size of the computer round-off errors depends on the thermodynamic state. For the two-dimensional nearest neighbor interaction lattice gas, this effect depends on the temperature but apparently not on the density. This is illustrated by the results in Table 5.5. These results are for $u/k_B T = -0.7$ and $\rho = 0.5$. For the results in Columns I and II, the lowest numerical precisions used were REAL*4 and REAL*8, respectively. The results in Column III are from the analytic solution of the two-dimensional nearest neighbor interaction lattice gas¹¹ at $\rho = 1/2$. These results are exact. For this lattice gas, exact results are available only for $\rho = 0, 1/2$, and 1. Comparison of results in Columns I and II with results in Column III shows that the numerical results are accurate through three significant figures.

The results discussed above are based on a set of exact equations. The results indicate

Table 5.5

$g^{(2)}(x, y)$ for the two-dimensional nearest neighbor interaction lattice gas. $u/k_B T = -0.7$ and $\rho = 1/2$. Column I: REAL*4. Column II: REAL*8. Column III: Exact results.

x	y	I	II	III
0	0	-0.0058	-0.0058	0
1	0	1.1825	1.1820	1.1843
1	1	1.0615	1.0611	1.0639

that these equations may be solved to any specified accuracy when the numerical work is done with corresponding precision. The only apparent limitation on accuracy is computer round-off error. This limitation can be overcome with improved computer hardware or software. The main limitations on the Flory-Huggins method apparently result from assumptions about the particle distribution functions. The approach discussed here eliminates any need to make assumptions about the particle distribution functions. Results indicate that they can be calculated as accurately as desired. The approach will facilitate a thorough examination of such questions as the effects of the shape of polymer molecules and of "free volume" on thermodynamic properties.

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5.2.5. Neutron and X-Ray Diffraction Study of the Metallic Glass $Ti_{84}Si_{16}$

(P. Lamparter,¹ A. Habenschuss,² A. H. Narten)

The total structure functions of amorphous $Ti_{84}Si_{16}$ have been evaluated by neutron as well as by x-ray diffraction. From combinations of

these two data sets, the Ti-Ti and Ti-Si atom pair distribution functions have been derived. The distances and coordination numbers thus obtained show that the short-range order is characterized by chemical bonding between the Ti and Si atoms. On the basic assumption that in metal-metalloid glasses there is no metalloid-metalloid nearest neighbor contact, the density-concentration correlation functions are discussed, and it is shown that besides the chemical ordering effect, there is a marked size effect in amorphous $\text{Ti}_{84}\text{Si}_{16}$. The results of this study are compared with those of other metal-metalloid glasses, and common features of this type of amorphous alloys are shown.

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5.2.6 Chemical Dynamics of Molecular Processes

5.2.6.1 Theoretical Investigation of Vibrational Energy Transfer in Polyatomic Molecules (D. W. Noid, S. K. Gray,⁹ S. A. Rice¹⁰)

In a recent paper we demonstrated, via a numerical analysis, the likelihood of fractal behavior¹ in the classical dynamics of atom-diatom collisions when long-lived complexes occur. We focused attention on the so-called chattering regions, first noted in collinear reactive scattering,² which generate apparent erratic behavior when a final condition such as product vibrational action or energy is plotted against an initial condition such as initial vibrational phase angle.

Surprisingly, at least for chattering associated with nonreactive (but inelastic) collisions, Gottdiener³ showed that within these regions there exists an infinite number of smooth, regular subdomains (which we term icicles) and an infinite number of point discontinuities. Our results corroborated Gottdiener's observations for a different scattering system and further characterized this curious mathematical behavior as being

fractal in the sense that the dimension of the function in the chattering region is not always one, which is the ordinary (non-fractal or Euclidian) dimension of well behaved functions. We also found that the presence of icicles, at least for the collision energy studied here, leads to an initial fast decay of the survival probability of the complexes; however, the behavior over a longer and wider time range is roughly characterized by a single, more slowly decaying exponential.

The system we studied was a T-shaped model for $\text{He} + \text{I}_2$ collisions introduced by Beswick, Delgado-Barrio, and Jortner;⁴ the same system has been studied by us in the context of van der Waals vibrational dissociation.⁵ The model has two coupled Morse oscillators and the specific parameters and masses used can be found in Ref. 5. The diatomic molecule initial conditions were determined from the appropriate I_2 Morse oscillator action-angle expressions as given by Rankin and Miller.² The vibrational action J_1 is always fixed at 29, which means the diatomic molecule always has an initial energy corresponding to an I_2 quantized vibrational energy level of $v = 29$. Q_1 is varied between 0 and 2π , corresponding to a sampling of all allowed vibrational phase angles. At the end of each trajectory, the final vibrational action, J_f , is computed from the same Morse oscillator formulae. The function of interest is $J_f(Q_1)$.

Figure 5.11.a shows the result of scanning the initial vibrational phase Q_1 over the full $(0, 2\pi)$ range with a 0.001 radian step size. The function $J_f(Q_1)$ appears very regular, forming the locus of points on a differentiable function except in the chattering region, $3.7 < Q_1 < 5.7$. In this region, one sees many subdomains of regular behavior, the icicles, separated by domains of apparent erratic behavior. Figure 5.11.b shows a blow-up (in steps of 2×10^{-5} radians) of the region between 4.5 and 4.7 radians. Icicles separated by domains of erratic behavior can be seen at all levels of magnification of Figure 5.11. Thus, magnification of any apparent erratic domain between

Fig. 5.11.a. The entire range of final vibrational action J_F vs. initial vibrational phase Q_1 .

Fig. 5.11.b. A magnification of the central portion of the chattering region.

any two icicles leads to more icicles and erratic domains and so on. The chattering region here is thus not merely a complicated but differentiable function; rather, it is a function for which there is no smallest scale; i.e., for which repeated magnification as shown in Figure 5.11 reveals finer and finer levels of detail. This property of self-similarity defines a fractal curve. Of course, it might

be argued that we have not explicitly demonstrated this because we have only examined a few magnifications of the chattering region. It is with this criticism in mind that we calculate the fractal dimension, which is a more concrete measure of the fractal nature of a function.

The concept of a fractal curve is not new; Weierstrass' function of 1872 is just one

famous and old example.⁶ The fractal dimension is defined as⁷

$$d_F = \lim_{\epsilon \rightarrow 0} \frac{\ln N}{\ln(1/\epsilon)} \quad (1)$$

where N is the number of squares or bins of length ϵ that the function passes through when the two-dimensional space of range and domain is divided up into a grid of such squares. Given (1), it is easily verified that a point has $d_F = 0$ because only one bin of arbitrary size ϵ covers a point. An ordinary line has $d_F = 1$, since the number of bins covering a line is equal to $(1/\epsilon)$. If $d_F > d_{\text{Euclidian}}$, then one has a fractal. For a curve, $d_{\text{Euclidian}} = 1$. Practically, the fractal dimension is determined as follows. Let N_ϵ be the number of bins of size ϵ along, say, the Q_1 axis. Since $N_\epsilon \sim 1/\epsilon$, it is clear from Equation (1) that as $\epsilon \rightarrow 0$ (or $N_\epsilon \rightarrow \infty$), a plot of $\ln N$ vs $\ln N_\epsilon$ will tend to a straight line of slope d_F . We note that the concept of dimension is very useful in understanding several aspects of nonlinear dynamics;⁷ in previous work, it has been possible to use it to calculate the number of integrals of motion for a three-oscillator model.⁸

We have chosen three regions to investigate the dimensionality of $J_F(Q_1)$. Consider first the regular region $0 \leq Q_1 \leq 0.8$. From these data, the dimension d_F is calculated by simple differencing; it is found to be very close to 1, as it should be.

The second region we have chosen to investigate is that shown in Figure 5.11.b, namely $4.5 \leq Q_1 \leq 4.7$. Table 5.6 displays the results obtained when 9600 points are used to represent $J_F(Q_1)$. It was clear that d_F is significantly different from 1 and is, in fact, close to its possible upper limit, 2. It is also important to realize that the total number of grid points is $N_\epsilon \times N_\epsilon$ and that for the calculation to be meaningful this number must be much greater than the number of points used to represent the function.

Table 5.6

Calculation of d_F for $4.5 \leq Q_1 \leq 4.7$ using 9600 points to represent $J_F(Q_1)$.

N_ϵ	N	d_F
5	25	2.00
10	100	2.00
15	225	1.99
20	399	1.94
25	615	1.90
30	869	

The third region for which we have estimated d_F is $4.5 \leq Q_1 \leq 4.52$. The results obtained are shown in Table 5.7. This calculation used 3600 points to represent the function in the specified region and is therefore not as reliable as the calculation leading to the entries in Table 5.6. Nonetheless, d_F is still found to be, without doubt, substantially different from 1 and closer to 2.

The calculations described above show that finite portions of $J_F(Q_1)$ in the chattering region of an inelastic collision have $d_F > 1$. Moreover, different ranges within the chattering region may have different values of d_F , all of which deviate from unity except for regions corresponding to only portions of icicles,

Table 5.7

Calculation of d_F for $4.5 \leq Q_1 \leq 4.52$ using 3600 points to represent the function.

N_ϵ	N	d_F
5	25	2.00
10	100	1.95
15	223	1.90
20	386	1.86
25	571	

which obviously will have $d_F = 1$. Indeed, the fact that d_F is closer to 2 than to 1, which value of fractal dimension corresponds to an area, indicates, at least in the regions examined, that $J_F(Q_I)$ is almost area filling, a result that supports the use of statistical theories to approximate the dynamics in these regions but does not substantiate use of statistical theories to approximate the dynamics in the entire chattering region. Note that each icicle of Figure 5.11 correlates with a region where there are a fixed number of complex vibrations. More remarkably, within every gap between the one vibration regions is a similar pattern of two vibration regions, and so on, ad infinitum. Thus, the beginning and end of each icicle, in addition to being a point of discontinuity in $J_F(Q_I)$, is an infinite-lived trajectory. In a small region, about each point of discontinuity we expect very erratic behavior indeed, since close to each such point one can find trajectories associated with an arbitrary (large) number of complex vibrations! There is, therefore, a remarkable element of chaos in the class of problems represented by our model, for we now expect to find essentially infinite-lived trajectories in parts of the chattering regions. We note that Gottdiener³ inferred much of this strange behavior despite his work preceding the widespread discussion and development of the role of chaos and fractals in multidimensional systems (and with limited computational resources).

To conclude, a remarkable pattern of self-similar structure in these structures was found in the chattering region of simple inelastic atom-diatom collisions. This structure has fractal character. The dynamics in the chattering region, despite the presence of very "chaotic" trajectories, can contain a non-statistical component due to large icicles.

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9. Department of Chemistry, The University of Chicago.
10. James Franck Institute, The University of Chicago.

5.2.6.2 Semiclassical Calculation of Excited States in Polyatomic Molecules

(D. W. Noid, R. A. Marcus⁵)

In a recent article,¹ we demonstrated that the "trajectory-close method" applied to 1:1 and 2:1 resonances^{2,3} can be used to treat in a simple but general way arbitrary classical resonances, within the exact WKB (i.e., the Einstein-Kramers-Brillouin) semiclassical approximation. The only requirement is that the trajectories be quasiperiodic. The method was illustrated using 3:1, 3:2, 5:2, 4:1, and 5:1 resonances for two-coordinate systems. The results supplement our earlier study of 1:1 and 2:1 resonances and of a 3:1 resonant avoided crossing problem.⁴ The resulting eigenvalues and eigentrajectories were compared with their quantum mechanical counterparts.

The Hamiltonian used for the $n:m$ resonances is:

$$H = 1/2(p_x^2 + p_y^2 + \omega_x^2 x^2 + \omega_y^2 y^2) - a(x^3 + y^3) + bx^m y^n + cx^2 y^2. \quad (2)$$

This Hamiltonian was chosen because its simplicity permits an accurate quantum mechanical variational calculation of the eigenvalues.

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The semiclassical trajectory-based method is readily used, on the other hand, with much more complicated Hamiltonians. In a resonance with $\omega_x = n$, $\omega_y = m$, the resonant coupling term is $b x^m y^n$. An example of the trajectories for these systems is given in Figure 5.12, which also serves to identify the difficulty in finding useful analytical coordinate systems for new cases. The cross-section line used for joining the two ends of a cycle of the trajectory, as well as for calculating an independent phase integral, is given below. This second phase integral is (in units of $\pi = 1$)

$$\oint p_1 dq_1 = 2\pi(n_1 + 1/2) . \quad (3)$$

For an eigentrajectory, n_1 is the integer. The total phase integral along one cycle of the trajectory, the ends joined, is given by

$$\oint p_1 dq_1 = 2\pi N + (n + m)\pi , \quad (4)$$

where N is the principal quantum number for the state, an integer, and the $(n + m)\pi$ term arises

because the trajectory touches the caustics of the figure $2(n + m)$ times during one cycle; there is a loss of phase $\pi/2$ each time, which must be included in semiclassical quantization. The phase integral in the l.h.s. of Equation (4) includes a portion from joining the ends of the trajectory on the line used for the integral in Equation (3). For the $(n = 3, m = 1)$ resonances, the Poincaré surface of section chosen for Equation (4) was for $y = 0$.

For the states in Table 5.8, EBK semiclassical quantization could be used. The agreement in each case is, in absolute terms, seen to be very good. All of these states were degenerate in zeroth order.

The present method is restricted to a few coordinates, but its advantage in that case is that, among EBK-type semiclassical methods, it is an exact method without further approximations. Indeed, a point which is worth stressing is that the present surface of section method is extremely simple to use, is readily applied to a wide variety of potentials,

Table 5.8
Quantum and Semiclassical Eigenvalues

Resonance (n,m)	State ^a (N_2, n_1)	State ^b (order)	E_q^c	E_{sc}
(3,1)	(3,0 ⁻)	4	4.977	4.976
	(3,0 ⁺)	5	5.015	5.009
(4,1)	(4,0 ⁻)	5	6.494	6.492
	(4,0 ⁺)	6	6.503	6.502
(5,1)	(5,0 ⁻)	6	7.999	7.999
	(5,0 ⁺)	7	8.000	8.001
(3,2)	(6,0 ⁻)	6	8.499	8.500
	(6,0 ⁺)	7	8.506	8.505
(5,2)	(10,0 ⁻)	9	13.494	13.499
	(10,0 ⁺)	10	13.501	13.501

^aThe minus denotes the member of the degenerate pair with lower energy.

^bThe states are ordered by energy, the lowest state being the ground state, and all states lower in order than the cited ones being non-degenerate.

^cQuantum variational calculation.

Fig. 5.12. 3:1 Resonant classical trajectory for state (3,0) in Table 5.8. Parameters used were $\omega_x = 3$, $\omega_y = 1$, $a = 0.005$, $b = 0.05$, and $c = 0.01$.

polynomial or otherwise, and has been shown through many tests to be accurate within the framework of the EBK approximation. Its main limitation is that at present it is readily applied only to 2D and 3D coordinate systems.

The trajectory-close method was found to treat systems containing internal resonances and is exact within the primitive semiclassical (i.e., EBK) approximation.

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 2. D. W. Noid and R. A. Marcus, J. Chem. Phys. 67, 559 (1977).
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6.0 CHEMISTRY OF TRANSURANIUM ELEMENTS AND COMPOUNDS

Studies are made in this program to enhance our understanding of the role of 5f electrons in chemical bonding. Most of our studies on the macroscopic scale emphasize certain isotopes available from the National Transplutonium Production Program centered at HFIR/TRU - namely, ^{248}Cm , ^{249}Bk , ^{249}Cf , ^{253}Es , and ^{254}Es . Particular classes of compounds, such as hydrides, chalcogenides, and pnictides are often selected for study on the basis of their utility in bringing out significant chemical differences between the lanthanides and the actinides. High temperature/high pressure experiments on actinide metals and compounds reveal characteristics about the degree of 5f electron localization as a function of atomic number in the series. Magnetic properties of metals and compounds are investigated using ultra-sensitive methods and hydration numbers of ions in solution are investigated by neutron scattering at HFIR. As a result of a recently renewed multi-laboratory effort involving four national laboratories, experiments are now being formulated to investigate further the chemical properties of elements 101-105 on a "one-atom-at-a-time" basis. Since relativistic effects increasingly modify chemical behavior as one proceeds to heavier elements, ideas and calculations from relativistic quantum theory are employed to suggest experiments. Initial chemical methodologies to be applied in this latter work include solvent extraction, ion exchange, electrochemistry, and gas chromatography. Collaborative nuclear studies, primarily with targets of ^{254}Es , also are carried out with other national laboratories in efforts to discover new isotopes of elements 101-105 of utility in chemical experiments or to improve the yields of known isotopes of these elements.

6.1 Transeinsteinium Chemistry

6.1.1 Possible Relativistic Chemical Behavior in Elements 103-105

(O. L. Keller, Jr.)

Strong relativistic effects on the 7s and 7p orbitals may alter the chemical behavior of lawrencium (Lr), rutherfordium (Rf), and hahnium (Ha) from that expected on the basis of a simple extrapolation in the periodic table.¹ At the juncture of the actinides and transactinides in the periodic table (Fig. 6.1), the effects of relativity could cause the 7p_{1/2} orbitals to replace the expected 6d orbitals. Because their orbital symmetry is spherical in the relativistic limit, the 7p_{1/2} electrons can spend a high proportion of their time near the nucleus where they are accelerated to velocities near the speed of light. On the other hand, the symmetry of the d orbitals allows them to spend only a relatively small proportion of their time near the nucleus, and their behavior will be changed mostly indirectly by relativistic effects through the increase in shielding from the contracted s and p_{1/2} electronic orbitals.

The probability that relativistic effects cause qualitative changes in the electronic configuration in Lr is supported by the theoretical work of Desclaux and Fricke² and of Brewer.³ The calculations by these investigators indeed do give the ground state of Lr as 7s²7p_{1/2} instead of the 6d7s² configuration expected by analogy to the 5d6s² configuration of Lu. Extrapolating from these Lr results, it might also be predicted that Rf could have the configuration 7s²7p_{1/2}² instead of the 6d²7s² analogous to the 5d²6s² of Hf and that Ha could be 6d7s²7p_{1/2}² instead of 6d³7s² as expected by analogy with Ta.

It appears on the basis of our current knowledge that the heats of sublimation, ΔH_{sub} , and the ionization potentials, IP, will be the most sensitive of the ordinary chemical thermodynamic quantities to these relativistic effects. But neither one of these quantities is amenable to direct measurement with the few atom quantities that will ever be available for these elements. In the case of the IP's, relativistic Hartree-Fock programs, such as those of

IA												VIII					
1	H																
2	Li	IIA											III	IV	V	VI	VII
3	Be												6	7	8	9	10
4	B												Al	Si	P	S	Cl
5	Na	IIA	III	IV	V	VI	VII	VIII	IB	II	III	IV	V	VI	VII	VIII	IX
11	Mg												13	14	15	16	17
12													Ga	Ge	As	Se	Br
19	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn					
20																	
21	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I
22																	
23	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At
24																	
25	Fr	Ra	Ac	Rf	Ha	106	107	108	109	(110)	(111)	(112)	(113)	(114)	(115)	(116)	(117)
26																	(118)

**LANTHANIDE
SERIES**

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
58	59	60	61	62	63	64	65	66	67	68	69	70	71

**ACTINIDE
SERIES**

Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
90	91	92	93	94	95	96	97	98	99	100	101	102	103

Fig. 6.1. Modern periodic table with undiscovered elements 110-118 shown in their expected positions.

Desclaux⁴ and Grant⁵, will have to be refined to the point that they can be used with confidence to make reliable calculations of the first 3 ionization potentials of Lr, for example, for use in the Born-Haber cycle. Although ΔH_{sub} cannot be measured directly, Zvara and coworkers⁶ have shown that under certain experimental conditions it can be estimated from the gas chromatographic separation of elemental actinide atoms on a Ti chromatographic column. Some results from Zvara's laboratory in Dubna are given in Figure 6.2 which shows that metallic Fm and Md behave divalently in the same manner as Yb and Es. The limitations of the method are indicated by the fact that Cf and Sm, which have the same ΔH_{sub} 's, appear at slightly different places in the column.

Actually we are not interested in the ΔH_{sub} 's of Lr, Rf, and Ha as such but in

their capacity to signal the appearance of relativistic effects on the electronic configurations. The seemingly low heat of adsorption, ΔH_{ads} , for californium is encouraging from this point of view because it indicates that a 5f electron has not been promoted and mixed into the d and s levels in the adsorption process on Ti - although this promotion does occur in going from the divalent atoms of Cf vapor to the trivalent metal. This result from Zvara and coworkers is important because the promotion of the $7p_{1/2}$ electron in Lr, for example, to a 6d would destroy the opportunity to detect the ground configuration predicted by the theorists even though they might be correct.

On the basis of the results from Dubna given above we can assume that ΔH_{ads} can be made proportional to ΔH_{sub} . This allows us to predict a very different ΔH_{ads} for Lr, for

Fig. 6.2. Illustrative results of thermochromatography, I. Zvara and co-workers, Dubna: elemental Cf, Es, Fm, and Md in titanium columns.

example, if it is a "p" element rather than a "d" element. In Table 6.1 the ΔH_{sub} 's for elements analogous to Lr as a "p" element are compared to those elements analogous to Lr as a "d" element. The conclusion is that the ΔH_{ads} for Lr would be very much lower than that for Lu if Lr is a "p" element, but approximately the same if it is a "d" element. Similarly the ΔH_{ads} of Rf should be

Table 6.1. Gas Chromatography of Lr⁰

A. Extrapolated heat of sublimation of Lr as a "p" element

Reference Element	$\Delta H_{\text{sub}}^{298}$ (eV)	Configuration
Ga	2.96	$3d^{10}4s^24p$
In	2.39	$4d^{10}5s^25p$
Tl	1.86	$5d^{10}6s^26p$
(Lr)	(1.4)	$5f^{14}7s^27p$

B. Extrapolated heat of sublimation of Lr as a "d" element

Gd	4.11	$4f^75d6s^2$
Cm	3.99	$5f^76d7s^2$
Lu	4.29	$4f^{14}5d6s^2$
(Lr)	(4.1)	$5f^{14}6d7s^2$

very much lower than that of Hf if it has a $7p_{1/2}^2$ configuration. In fact under these circumstances the ΔH_{ads} of Rf should be similar to Pb which has a $6p^2$ configuration. Thus the chemical effects of the appearance of the $7p_{1/2}$ shell in preference to the 6d should be detectable by the gas chromatography of the atomic species.

Many other experiments based on gas chromatography, solvent extraction, and ion exchange would be possible with these elements if sufficient quantities of them could be produced. Such an increase in production over present capabilities would be possible if a 40 μg target of Er^{254} could be made available. It is thought from a technical point of view that the production of such an Es target at the HFIR/TRU is possible. This target would allow experiments such as those outlined above (and more completely in reference 1) to be carried out and would thus allow us to map out the architecture of the periodic table in the critical region where the actinides join the transactinides.

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6.1.2 A Micro Mixer-Settler for the Rapid Solvent Extraction of Radioactive Nuclides (J. Halperin, J. H. Oliver, W. J. McDowell)

The usefulness of mixer-settlers for the mixing and separation of aqueous and organic phases is well established.¹ We are interested in the continuous processing of volumes of solution much smaller than usually considered for such a device - namely 1 to 2 cm³. This interest stems from potential applications to the study of elements 101-105 (made in accelerators on a few-atom-at-a-time basis). For laboratory procedures that require such small volumes and also relatively short throughput times, such a micro mixer-settler appears to have advantages over other approaches requiring larger volumes such as pulse columns and centrifuges. Here we report on such a system for the application to chemical separations and assays of short-lived radioisotopes; especially for short-lived alpha-particle emitters where smaller volumes will simplify sample preparation for alpha-counting.

In this design, the mixer and the settler sections have been separated into two distinct parts. The mixer section is a cell into which the organic and aqueous streams are introduced, and which is isolated by short lengths of flexible small-bore tubing. Mixing is achieved by contacting the cell with a vibrating device using a clamping

arrangement to hold the cell in place. The Vibratory Mixer has the advantage of not requiring the placement of components such as stirrers or magnetic stirring bars within the mixing cell. Further, it appears to be especially effective at rapidly breaking up the aqueous-organic mixture into minute globules which are necessary in order to present high interfacial areas for effective and rapid transfer of chemical moieties across the phase boundary.

In the current design, we make use of a cylindrical mixing cell (~9 mm ID, ~12 mm long). The cell is partitioned with a 1 mm wall in which a number of small holes have been placed. The partition is displaced from center so that one chamber is up to twice as large as the other. The partitioned cell provides significantly better mixing than one that is not partitioned. This is due to the fact that passage from the first and larger section of the cell is delayed (allowing more time for interphase transport of chemical species) before entering the second chamber of the cell where exit from the mixing cell proceeds.

The settler cell consists of a cylindrical cavity containing two conical sections (one of which is inverted). The heavy (usually aqueous) phase exits through the lower cone and the lighter (usually organic) phase through the upper. The phase disengagement region is maintained in the center between the two cones by flow rate adjustments on one or both streams. The internal volume of the settler is adjusted to ~1 cm³ or less; flow rates up to ~10 cm³/min can be readily maintained while yielding good phase separation. This requires continuous observation with timely adjustments to flow rate.

We have used two peristaltic pumps (e.g., Buchler Polystatic) in these experiments to independently adjust the flow rates for the aqueous and organic streams. The two pumped streams are joined in a "Y" or "T" using capillary tubing and then passed as a single stream to the mixing cell. Because the

system operates at low pressures, friction fits of capillary tubing to the various parts serves to firmly hold all lines intact.

We have used the system bis(2-ethylhexyl)-phosphoric acid (HDEHP)² in n-heptane to evaluate rare earth extractions in the micro mixer-settler. Concentrations of HDEHP in the millimolar range have been contacted with 0.05 M KNO₃ aqueous solutions adjusted to pH = 1.5 with HNO₃. We have used 129-day ¹⁷⁰Tm tracer and a sodium iodide counting system to measure distribution coefficients for these organic extractions. Initially a series of batch measurements was carried out to provide a reference time frame to compare mixer-settler results. In these experiments 1 ml aliquots of stock solutions of both the organic and aqueous (with tracer) phases were contacted in a small vial. The organic phase was carefully introduced above the aqueous phase to minimize mixing. The capped vial was then manually held in contact with the vibrating mixer for a timed interval, following which the dispersion rapidly separated into two bulk phases. To obtain the batch data, the vial was centrifuged and aliquots of each phase were withdrawn for assay. The distribution coefficients, D(org/aq), for these batch experiments were thus evaluated as a function of mixing time. Typically, distribution coefficient values close to equilibrium were achieved in the 15-30 second range. Assuming first-order kinetics for the rare earth transfer across phase boundaries, we estimate 5 ± 2 sec half-times for these batch transfers. In experiments in which organic and aqueous (with tracer) streams were passed through the micro mixer-settler, the distribution coefficient was evaluated as a function of flow rate. If we take the mean residence time in the mixer as the ratio of the volume of the mixer cell to that of the flow rate, we may compare mixing times in the mixer-settler to those observed in the batch experiments. Distribution coefficients approximating equilibrium coefficients were

typically observed in the 20-40 second range. We have estimated the half-time for transfer of Tm across the phase boundary at 7 ± 2 seconds, somewhat greater than in batch extraction.

A device such as the one described here appears suitable for the solvent extraction separation of short-lived nuclides produced by accelerator bombardments or in nuclear reactors, and their separation into small volumes for chemical identification and characterization. Similarly it may be applicable to the evaluation of distribution coefficients in the study of short-lived actinide and lanthanides.

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6.1.3 A ²⁵²Cf-Helium Jet System to Provide a Source of Short-Lived Fission Fragments (J. Halperin)

The ability to study the chemistry of the heaviest elements (i.e., $Z \geq 101$) is closely tied to access to appropriate ion-accelerators. These very heavy elements cannot be prepared in nuclear reactors from light actinides by successive neutron capture and beta decay due to competition from fission. This propensity to fission effectively limits the maximum atomic number for reactor produced nuclides to $Z = 100$. Research and development into chemical techniques for carrying out studies with these heaviest elements (i.e., $Z \geq 101$) is closely tied to their one-atom-at-a-time production mode and their subsequent introduction into a chemical medium. Because access to ion-accelerators for the

development and perfection of such techniques is limited, we have arranged to simulate radionuclide production at the accelerator with a ^{252}Cf source.

Current techniques for the production of these heavy nuclides involve heavy-ion beams impinging upon a heavy element target to produce the reaction product(s) of interest. These product nuclides produced one-atom-at-a-time with multi-MeV kinetic energies are typically stopped in a chamber pressurized with helium gas and then carried down capillary tubing to a more distant receiving chamber which is held at a lower pressure so that a stream of gas flows between the two chambers (i.e., a helium jet).¹ Chemical procedures are designed to collect heavy element atoms and to incorporate them into an appropriate medium in preparation for particular chemical experiments. Since radioactive lifetimes for these nuclides are typically very short, requiring fast chemical procedures, there exist incentives to devise continuous procedures and to automate them as much as possible.

^{252}Cf , because of its high spontaneous fission decay rate, is an especially useful source for a variety of nuclides (i.e., fission products). Relatively high yields of a number of rare earth isotopes are produced in ^{252}Cf spontaneous fission and these can serve as stand-ins for developing chemical procedures for actinide experiments.

The present design provides for a cylindrical chamber in which the ^{252}Cf source is introduced at the end of a rod into the chamber on the cylinder axis. The chamber is pressurized with helium gas and is large enough to provide an average path length of ~ 7.5 cm so as to stop fission fragments within the gas volume before striking container walls. The helium gas is seeded, prior to being passed into the chamber, with micron-size particles of KCl to provide a substrate to which fission fragments can attach. By seeding, collection yields for these ion particles can be made to exceed

90%. The seeding is accomplished by passing the helium gas over a bed of KCl in a quartz container heated to 600–650°C. The gas is then passed through a filter or alternatively a length of tubing to allow larger size KCl aggregates to drop from the stream by gravity.

The collection chamber is a modification of a design due to McDowell.² The helium jet impinges within the chamber against a gritted frit through which there is a continuous flow of an appropriate solution in which the chemical moieties have been found to be soluble. This solution drains to a reservoir which then serves as the source for chemical experiments. The system described here lends itself to continuous operation and can in turn be linked to further continuous and automatic chemical operations.

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6.1.4 New Results Concerning Heavy Md Isotopes Produced in Heavy-Ion Bombardments of ^{254}Es

(R. L. Hahn,¹ E. K. Hulet,¹ R. W. Loughheed,¹ J. F. Wild,¹ R. J. Dougan,¹ K. J. Moody,¹ C. M. Henderson,¹ R. J. Dupzyk,¹ K. Summerer,² G. Bethune³)

As noted previously,⁴ because of our interest in finding new isotopes that might be of use in studies of transeinsteinium-element chemistry, we have been collaborating with colleagues at LLNL in studies of the radioactive products of heavy-ion bombardments of ^{254}Es . These bombardments have been done at the 88-inch cyclotron at LBL.

Significant new results have been found in these experiments concerning the decay of

heavy Md isotopes. It is noteworthy that these experiments would probably not have succeeded except for two major factors: (1) the development at the 88-inch cyclotron of a new, external ion source, the electron cyclotron resonance (ECR) source, and (2) the availability of an isotope separator in an α -containment facility at LLNL. The ECR source, in vivid contrast to cyclotron operation with the previously used, internal PIG source, allowed us to irradiate the target for many hours with stable beams of ^{22}Ne and ^{18}O , at relatively high intensities, ~ 2 (electric) μA . The isotope separator allowed us to separate by mass the different radioactive isotopes produced in these irradiations. By using a helicopter to fly the recoil catchers containing the produced radioactivities from LBL to LLNL, we were able to have mass-separated samples ready for counting about one hour after the end of bombardment (eob). This mass separation was very important in that it provided us with relatively pure samples of the isotopes of interest, free of the prohibitively large interferences caused by other radioactive products and the ^{254}Es "knock-over" nuclei that were present in the recoil catcher. And the rather short delay between eob and the start of counting enabled us to observe the decay of isotopes such as 1-hr ^{258}Md and 1.6-hr ^{259}Md .

6.1.4.1 Experimental Verification of the Electron-Capture Decay of ^{258}Md to ^{258}Fm

The existence of the nuclide, ^{258}Md , was first reported in 1980.⁵ Its half-life was reported as 43 min, and it decayed by spontaneously fissioning (SF). As indicated in Ref. 5, the observed SF activity was "presumed" to be that of the ^{258}Fm daughter (half-life of 380 μs), produced by electron-capture decay (EC) of the ^{258}Md parent. While this assumption was quite plausible based on our knowledge of nuclear structure in the heavy elements, it was also conceivable⁵ that ^{258}Md itself decayed by SF.

In Ref. 5, it was also noted that an attempt was made to use chemical means to identify the 43-min activity as an isotope of Md, but was unsuccessful. Thus, no direct identification of (the atomic number of) ^{258}Md has been reported.

It is also noteworthy that, while Ref. 5 presented very interesting data on the systematics of SF of heavy Cf and Fm nuclides, the SF results for ^{258}Fm (from the decay of ^{258}Md) required substantial corrections for the presence of another SF nuclide, ^{256}Fm (with half-life of 158 min); since only 35% of the observed fissions in Ref. 5 were attributed to ^{258}Fm , it is possible that some properties of the ^{258}Fm SF decay were obscured by the ^{256}Fm .

The present work with mass-separated ^{258}Md avoids - or at least reduces to the level of only a few percent - the problem of contamination by ^{256}Fm (and of 77-min ^{256}Md , which decays to ^{256}Fm). Thus, we were able to obtain reliable counting data and measure an accurate new value for the ^{258}Md half-life, namely, 65 min.

To prove experimentally that the 65-min isotope indeed decays by EC to ^{258}Fm , we devised a new experiment. Because the EC process forms a vacancy in an inner electron shell, often in the K shell, the process has as its signature the emission of (K)X rays. A sample containing the mass-258 sample from the isotope separator was placed in a specially constructed chamber, such that fission fragments and X rays could be simultaneously detected with high counting efficiency. The data so obtained were then analyzed to search for correlations in time between the emitted X rays and fission fragments. Figure 6.3 presents the results of our first experiment; several more runs, with analogous results, have since been done to improve the counting statistics. The figure shows the spectrum of K-X rays that precede the emission of fission fragments. The spectrum is clearly and uniquely that of the K-X rays of Fm.⁶ This experiment also

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Fig. 6.3. Spectrum of X rays observed to precede, with a particular correlation in time, the SF decay of ^{258}Fm . This measurement proves that the 65-min parent of ^{258}Fm is ^{258}Md .

tells us the average time delay between the emission of the X rays and of the subsequent fission fragments, and so allows us to measure the half-life of the SF daughter that follows the EC decay. The half-life so determined, 355 μs , is in good agreement with the 380 μs value for ^{258}Fm . And finally, the measured kinetic energy spectrum of the fission fragments is quite characteristic of ^{258}Fm (see Section 6.1.5 below).

This observation of Fm K-X rays in a definite time correlation with the subsequent SF decay of ^{258}Fm (identified by its half-life and fission energy spectrum) definitively proves that the 65-min parent is ^{258}Md , since it decays by EC to the known nuclide, ^{258}Fm . In view of the uncertainties

that we have noted in the results of Ref. 5, the present work not only verifies the discovery claim but also constitutes the first unequivocal identification of ^{258}Md .

6.1.4.2 New Long-Lived Isotope, ^{260}Md

During the past few years, considerable effort has gone into measuring the cross sections of the trans-einsteinium nuclides produced in the nuclear reactions of ^{18}O and ^{22}Ne with ^{254}Es .⁷ One trend that has emerged from this work is that the mass-yield curves, i.e., plots of the cross sections vs mass numbers of the different isotopes of a particular element, have similar, Gaussian shapes for the different elements. Extrapolation of such curves to higher mass numbers then indicates that as yet unknown, neutron-rich isotopes of some of the elements above einsteinium should be observable. For example, the unknown isotope, ^{260}Md , was predicted to have a cross section of about 1 microbarn.

Estimates of the half-life of the odd-odd ^{260}Md gave values on the order of several days. Thus, this isotope was a likely candidate for our experiments in which the isotope separator at LLNL was used to produce samples of different atomic masses.

Our experiments (involving many irradiations done at intervals during a period of ~ 1 year) have indeed found a new radioactive nuclide with mass 260. The half-life is rather long, 32 ± 3 days. This large value, coupled with the high decontamination factors provided by the isotope separator against the large yields of lighter-mass radionuclides, ensured that our mass-260 samples effectively contained only one decaying isotope; thus, the analysis of the counting data was straightforward.

The measured cross sections for production of this new isotope, 320 nb for an ^{18}O beam at 10 MeV, and 298 nb for 126 MeV ^{22}Ne , are consistent with values from the extrapolated mass-yield curves for either ^{260}Md or ^{260}No . However, the even-even ^{260}No is expected to have a short half-life, and so should not be

observed under the conditions of our experiments. Thus, we assign this new radioactivity to ^{260}Md .

A striking characteristic of this isotope is that the only decay process observed to date is SF. A search for an α -decay branch for this isotope has yielded negative results, with an upper limit of a few percent. A further intriguing possibility that we have investigated is that the observed SF decay is not due to the long-lived odd-odd ^{260}Md , but to its even-even short-lived daughter; i.e., ^{260}Md might decay either by β^- emission to ^{260}No , or by EC to ^{260}Fm .

To resolve these questions, we have done experiments to look for the time-correlated decay of ^{260}Md preceding the SF events. For the possible β^- decay to ^{260}No , we searched for β^- particles preceding SF. While β^- particles were observed, their distribution in time was random with respect to the SF events. In other words, the nuclide that decayed by SF did not follow after the decay of a β^- emitting parent; thus, the decay route leading to ^{260}No was ruled out. Similarly, another experiment was done to investigate the possibility of EC to ^{260}Fm ; we searched for K-X rays (in the energy range of 90 to 140 keV) preceding SF, with the same equipment that had been successfully used to identify ^{258}Md . To date, no such K-X rays have been seen. While it is conceivable that ^{260}Md might have an EC decay energy that is below the binding energy of the K electrons in Fm, and so might produce L-X rays but not K-X rays, such a low decay energy would imply that the half-life for the EC decay should be much longer than the value of one month measured for ^{260}Md . Hence, it is considered unlikely that ^{260}Md decays by EC, and so it appears that the observed SF decay is that of the ground state of ^{260}Md .

Our discovery of this new heaviest isotope of Md is significant on at least two counts. First, ^{260}Md is only the second isotope known to contain 159 neutrons; the other is ^{259}Fm . We see that the addition of this 159th neutron imparts substantial extra stability

to the resulting nucleus: the half-life of ^{259}Fm is 1.5 s, while that of its neighboring isotope with 158 neutrons, ^{258}Fm , is only 0.4 ms; similarly, the respective half-lives of ^{260}Md and ^{259}Md are 32 days and 95 min.

Secondly, the SF properties of ^{260}Md are quite unusual, and have helped us to discover an unexpected, new property of the fission of the heaviest elements. This topic is discussed in the next section, 6.1.5.

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6.1.5 Bimodal Symmetric Fission Observed in the Heaviest Elements: A New Phenomenon

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Heavy-ion bombardments of ^{254}Ts at LBL followed by isotopic separation at LLNL have been used to produce relatively pure samples of 65-min ^{258}Md , 95-min ^{259}Md , and of the

recently discovered 32-day ^{260}Md (see Section 6.1.4). Because the contamination levels of other radionuclides, especially the SF nuclide ^{256}Fm , were greatly reduced in these samples, they were especially suited for studies of the SF characteristics of the heaviest elements.

By observing the two fission fragments that are emitted in opposite directions by the SF nucleus, we can determine the kinetic energies, and the masses, of the fission fragments (after neutron emission). Figs. 6.4 and 6.5 show the measured distributions of mass, and of total kinetic energy (TKE), respectively, that we obtained for the SF of ^{258}Fm (from the decay of ^{258}Md), ^{259}Md , and ^{260}Md . Also included in the figures are data from separate experiments done at LBL, for the very short-lived SF nuclides, 1.2-ms ^{258}No and 20-ms $^{260}\text{104}$. No isotope separation was possible in these latter experiments, so that contamination from ^{256}Fm was noticeable; in the ^{252}No case, 13% of the 441 SF counts observed were due to ^{256}Fm , while for $^{104}\text{260}$, 12% of the 341 events came from ^{256}Fm .

We note in Fig. 6.4 that: all of the five SF nuclides undergo symmetric mass divisions. Yet the mass distributions do differ for the different nuclides. Some of the distributions are narrower than others, but all of them have wings that extend from the central peaks to much higher and lower masses. The asymmetric mass splits so characteristic of SF of the lighter Fm nuclides, and of other actinide nuclei, e.g., Cf isotopes, are not apparent in these curves.

Especially interesting are the TKE distributions of Fig. 6.5. Upon examination of the curves for $^{260}\text{104}$, ^{258}No , and ^{259}Md , we conclude that the peaks all fall around 200 MeV, with some skewing to higher energies. But, upon examining the data for ^{258}Fm and ^{260}Md , we see a much different type of behavior: the distributions, which are very similar for both nuclides, peak at much

Fig. 6.4 Provisional mass distributions (not corrected for neutron emission) obtained from correlated fragment energies. A small contribution from ^{256}Fm has been subtracted from each distribution. The mass bins have been chosen to be slightly different for each nuclide.

higher energies, ~235 MeV, but are skewed on the low energy side. This skewing to lower energies only becomes apparent because we have relatively pure, mass-separated samples

Fig. 6.5. Provisional total-kinetic-energy distributions (not corrected for neutron emission). A small contribution equivalent to the known amount of ^{256}Fm has been subtracted from each distribution.

of the two isotopes, ^{260}Md and ^{258}Fm . Previous work on ^{258}Fm had clearly shown that its TKE distribution peaked at significantly higher energies than for most other nuclides, but the skewing was not apparent because it was masked by the presence of considerable

^{256}Fm contamination in the samples.⁴

Examination of the five TKE distributions leads us to a consistent explanation of all of the data: the measured curves are the results of the superposition of just two TKE distributions, one centered at ~ 200 MeV, and the other, at ~ 235 MeV. Thus, the observed skewing, at high energies for ^{258}No and ^{259}Md , and at low energies for ^{258}Fm and ^{260}Md , is simply the manifestation of these bimodal distributions. Decomposition of the measured TKE distributions into two Gaussian distributions gives very consistent results for all of the SF isotopes studied (even though the relative amounts of the two Gaussians may differ considerably from one nuclide to another); the resulting centroids are: 205 and 232 MeV for ^{258}Fm , 195 and 234 MeV for ^{260}Md , 203 and 235 MeV for ^{258}No , and 201 and 235 MeV for ^{259}Md (^{260}No has a single Gaussian shape, centered at 200 MeV).

The bimodal TKE distributions also help somewhat to explain the different symmetric mass distributions seen in Fig. 6.4. Analysis of the data shows that coincident fission fragments that have high TKE values, >220 MeV, also have sharp symmetric mass distributions, while those with low TKE's, <200 MeV, have very broad, rather flat, mass distributions.

Our conclusion that two different TKE distributions occur in the heaviest SF nuclides is a significant new result in the physics of nuclear fission. The symmetric mass divisions and high TKE values, which a few years ago were thought to be special characteristics of only the heaviest Fm nuclides,⁴ are shown to be the result of a more general trend in the heavy nuclides, although these properties are most prominent in ^{258}Fm and ^{260}Md (in our work, bimodal fission is seen for atomic number Z from 100 to 102, and neutron number, N , ≥ 156).

Since these two different fission TKE distributions occur concurrently in the same nucleus, we conclude that there are two possible, competitive pathways on the nucleus' potential energy surface that can

lead to fission. One, associated with the high TKE values and narrow mass distributions, we qualitatively ascribe to the strong shell effects associated with the symmetric breakup of the fissioning nucleus into fragments with $Z \approx 50$; the other, associated with lower TKE values and broader mass distributions, we ascribe to the behavior of the fissioning nucleus as a liquid drop (note that the energy centroids around ~ 200 MeV are consistent with values expected from the systematics of nuclear fission based on the liquid-drop model⁵).

Why these two pathways coexist for heavy SF nuclei, and why a particular nuclide chooses one pathway more often than the other (determining the relative contributions of the two TKE distributions in a given nucleus), are two important, unanswered questions that await theoretical explanations.

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6.1.6 Measurement of Neutron Cross Sections in the 144- and 145-Mass Region

(J. Halperin, C. W. Alexander,¹ J. B. Knauer,¹ R. L. Walker²)

The longest-lived isotope of promethium is the 17.7 year ^{145}Pm . It can be prepared in nuclear reactors by the irradiation of samples of ^{144}Sm . See Diagram 1.

Neutron cross sections in this region are poorly known, so that the estimation of yields under varying conditions of thermal and resonance flux in reactor irradiations cannot be made with any confidence. We plan to measure the neutron thermal cross sections and resonance integrals of ^{144}Sm , ^{145}Sm , and ^{145}Pm .

Highly enriched ^{144}Sm (>95%) has been obtained as a source material for these measurements. Experiments are planned in which samples of ^{144}Sm will be irradiated under carefully controlled conditions. Mass spectrometric determinations of the $^{144}, ^{145}, ^{146}\text{Sm}$ isotopic distributions together with measurements from neutron flux monitors will allow an evaluation of neutron cross sections. By making use of neutron filters such as cadmium, we can measure the sample response to both the thermal and resonance components of the reactor neutron flux spectrum so as to determine both thermal cross sections and resonance integrals.³

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2. Analytical Chemistry Division
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6.2 Chemistry and Physics of Metals and Compounds

6.2.1 Studies of Actinide Metals and Compounds Under High Pressure Using X-Ray Diffraction¹

(R. G. Haire, J. R. Peterson,² U. Benedict,³ J. P. Itie,³ C. Dufour,³ S. Dabos³)

Studies of transplutonium metals and compounds under pressure provide information about their electronic behavior and atom-atom interactions, generate data which define equations of state, as well as determine the phase behavior and basic properties of the materials. The behavior of the respective 4f and 5f electrons in lanthanide and actinide metals and their compounds is an active research area in modern solid state science.

In the past two years the high pressure behavior of the first four transplutonium metals was determined in collaborative efforts with the European Institute for Transuranium Elements, Karlsruhe, Federal Republic of Germany.⁴⁻¹⁰ These studies have employed a Syassen-Holzapfel-type diamond anvil pressure cell that has routinely allowed pressures of up to 60 GPa (0.6 million atmosphere) to be applied to the sample materials. The samples were analyzed as a function of pressure at ambient temperature using energy dispersive X-ray diffraction analysis. In addition to determining the phase behavior of these pure metals as a function of pressure, it was also observed that under pressure the metals ultimately transform to an α -uranium-type orthorhombic structure, which indicated that participation of their 5f electrons in the metallic bonding had occurred (delocalization of the normally non-bonding f electrons). The pressure required for the onset of delocalization varied with the metal being studied and in a qualitative fashion could be related with the electronic configuration of the metal. Both americium and californium metals formed an additional phase not observed with curium and berkelium metals. The appearance of these additional phases and

the behavior of alloys under pressure became the object of additional studies.

The crystal structure sequence observed as a function of pressure for several trivalent lanthanide and actinide metals is: hcp - Sm type - dhcp - ccp - distorted ccp - orthorhombic α -uranium. For the first four transplutonium metals, the sequence begins with the room temperature-normal pressure dhcp form of the metal. With curium and berkelium, the distorted ccp phase has not been observed and the ccp phase transformed directly to the orthorhombic phase with pressure. In the case of americium metal, what originally was believed to be a monoclinic structure has been recently shown to be a distorted ccp phase¹⁰, and americium metal under pressure has now been shown to follow the sequence listed above. Recently, studies on berkelium-californium alloys were carried out to examine the composition at which the distorted fcc phase would be encountered¹¹. These alloys were obtained directly from the decay of ²⁴⁹Bk ($\tau_{1/2} = 325d$) metal into ²⁴⁹Cf metal. Two Bk_{1-x}Cf_x ($x = 0.35$; $x = 0.60$) alloys were each studied up to a pressure of 47 GPa. The berkelium-rich alloy under pressure exhibited the same sequence of phases as pure berkelium metal, and did not exhibit a distorted ccp phase. In contrast, the californium rich alloy behaved like pure californium and a distorted fcc phase was observed between the ccp and orthorhombic phases. The unit cell volumes of these alloys as a function of pressure are shown in Figure 6.6, where it is apparent that the phase transitions prior to delocalizations occurred without a discontinuity in relative volumes. The dhcp $\rightarrow$ ccp transitions for the alloys (12 GPa for $x = 0.35$; 14 GPa for $x = 0.60$) were found to be intermediate to pressures noted for comparable transitions in the pure metals (Bk = 10 GPa; Cf = 17 GPa). This transition has been correlated to the variation in d-electron occupancy in lanthanide metals. The sharp decrease in the relative volumes at pressures above 34 GPa together with the appearance of the

Fig. 6.6. Relative volumes of $Bk_{1-x}Cf_x$ alloys as a function of pressure (a) $Bk_{0.65}Cf_{0.35}$; (b) $Bk_{0.40}Cf_{0.60}$.

α -uranium-type structure reflects the onset of 5f electron delocalization in the alloys. The data in Table 6.2 permit a comparison to be made of the transformation pressures and changes in relative volumes upon delocalization for the pure transplutonium metals and

the berkelium-californium alloys. The values in Table 6.2 for curium metal reflect the special situation of its half-filled 5f shell. The reason for the existence of a distorted ccp phase in some of these materials is not understood at the present time. Further investigations of americium-curium alloys will further clarify the existence of the distorted ccp phase.

The semi-metallic monpnictides and monochalcogenides are also scientifically interesting groups of compounds to study, as they are likely to exhibit valence instabilities and electronic transitions under pressure. For the initial investigations of such materials under pressure, the monpnictides were chosen over the monochalcogenides, since the latter compounds are very difficult to prepare on the microscale required for the transplutonium elements. For the monpnictide of a given actinide metal, in progressing down the pnictogen group (nitride, phosphide, arsenide, antimonide) the metal-metal distances are greatly increased and the interaction between the f-electrons and the p-band of the anion should be altered.

Table 6.2. Transformation Pressures and Relative Volumes Upon Delocalization for the Transplutonium Metals and Berkelium-Californium Alloys

Material	P(GPa)			$\Delta V/V$ upon Delocalization
	DHCP $\rightarrow$ CCP	CCP $\rightarrow$ Distorted CCP	Delocalization	
Am	9.5	13.5	23	$\sim 6\%$
Cm	23	-	43	$\sim 21\%$
Bk	9-10	-	32	$\sim 12\%$
$Bk_{0.65}Cf_{0.35}$	12	-	34	$\sim 16\%$
$Bk_{0.40}Cf_{0.60}$	14	20-29	35	$\sim 15\%$
Cf	17	~ 30	41	$\sim 16\%$

A study of the nitrides, arsenides, and antimonides of californium-249 and curium-248 under pressure was undertaken recently. The nitrides as prepared exhibited face center cubic (NaCl type) structures and there was no indication of a structure change under pressure. Additional analyses of these data will be necessary to determine if there is evidence to suggest that an electronic transition occurred under pressure. The bulk moduli derived for these nitrides were comparable to bulk moduli for the lanthanide nitrides, and much higher than the bulk moduli for curium and californium metals. X-ray data collected for the arsenides and antimonides under pressure are presently being analyzed. During the collection of energy dispersive X-ray data for these latter compounds, it was noted that some interference was observed due to the fluorescence of antimony and future studies will need to address this problem.

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6.2.2 Absorption Spectrophotometric Studies of Actinide Compounds Under Pressure¹

(J. R. Peterson², R. G. Haire, J. P. Young,³ G. M. Begun, U. Benedict⁴)

Studies of actinide compounds under pressure using solid state absorption spectrophotometry complement our high pressure X-ray studies (see Section 6.2.1). The goal of the spectrophotometric studies is to monitor the effect of pressure on actinide compounds using the spectral properties of the materials in the 300-1100 nm wavelength region. Since the absorbances of transplutonium materials in this wavelength region are due mainly to f-f transitions, any perturbations to the 5f electrons as a result of applied pressure may affect the absorption bands. Thus, structural or coordination changes, changes in the electron configurations, and/or the involvement of the f electrons in bonding brought about by the application of pressure potentially can be detected by changes in the absorption spectra of the material under pressure.

A diamond anvil cell designed for use with our microscope-spectrophotometer has been used for obtaining room temperature

absorption spectral data from lanthanide and actinide samples at pressures up to 20 GPa. Several performance tests were carried out initially using lanthanide compounds and the first studies with actinide materials were reported last year.⁵ With AmI_3 , it was found that a pressure of ~ 2 GPa at room temperature was sufficient to convert its hexagonal crystal form into an orthorhombic form and that the transformation could be followed spectrophotometrically.⁶

Additional studies were carried out on CfBr_3 under pressure. At least two crystal modifications of anhydrous CfBr_3 are known to exist, one being an AlCl_3 -type monoclinic form and the other a PuBr_3 -type orthorhombic form. Although it is possible to synthesize directly the monoclinic form of CfBr_3 , the orthorhombic form had previously been obtained only from the beta decay of BkBr_3 exhibiting its PuBr_3 -type orthorhombic form. However, we have now synthesized the orthorhombic form of CfBr_3 by applying pressure to its monoclinic form.⁷ In Figure 6.7 are shown room temperature absorption spectra of CfBr_3 as a function of applied pressure. By ~ 3 GPa, the monoclinic form has converted to the orthorhombic form, which is retained after release of pressure. This transformation is believed to relate to the relative packing efficiencies of the two crystal structures. Beck and Gladrow⁸ proposed an order of packing efficiency of lanthanide trihalide crystal forms with pressure as follows: AlCl_3 -type monoclinic (least efficient space filling) $< \text{BiI}_3$ (FeCl_3)-type rhombohedral $< \text{UCl}_3$ -type hexagonal $< \text{PuBr}_3$ -type orthorhombic (most efficient space filling).

In addition, studies of PuI_3 , CmI_3 , and CfCl_3 under pressure are currently in progress. Results of studies on the actinide compounds made to date have not shown that the application of pressure has forced the involvement of f electrons of these compounds in their bonding, as was found with the metals at higher pressures (see Section 6.2.1). Instead, the application of pressure

Fig. 6.7. Room temperature absorption spectra of CfBr_3 in two crystallographic forms (AlCl_3 -type) monoclinic; PuBr_3 -type orthorhombic) at various pressures.

brought about structural changes which involved a structure of a larger molecular volume changing to a crystal form with a smaller molecular volume.

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6.2.3 Thermochemistry and Enthalpies of Vaporization of Actinide Metals and Compounds

(R. G. Haire, J. K. Gibson)

One approach for obtaining thermochemical data for transplutonium metals and compounds is to measure their vapor pressures as a function of temperature, from which their enthalpies and entropies of vaporization may be derived. The experimental approach requires monitoring the effusate from a Knudsen cell containing the material being studied. In earlier collaborative studies with Los Alamos National Laboratory such measurements were made for the transplutonium elements through californium using multimilligram amounts of the pure metals. The scarcity of the transcalifornium elements coupled with the higher volatility expected for them require that the experimental

approach be modified. The initial vapor pressure studies on einsteinium, the next element after californium in the actinide series, were thus carried out using an einsteinium-ytterbium alloy.¹

We have initiated a series of studies of transplutonium alloys to further define the variables involved in determining the vapor pressure of a metal over such systems and relating it to that of the pure metal. From these initial studies it has been possible to confirm and extend the earlier results obtained for einsteinium metal. Using these techniques it should be feasible to derive both the vapor pressure as a function of temperature and the enthalpy of vaporization of fermium metal. Studies of einsteinium alloys are presently in progress and will be carried over into the next report period.

Preparations for initiating vapor pressure studies of actinide compounds using a Knudsen effusion technique are nearly complete. To identify the species present in the vapor in equilibrium with the actinide compound being studied, a dual range mass spectrometer (1-511, 2-1023 AMU) has been incorporated into the system. The mass transferred as a function of temperature will be determined with the mass spectrometer and/or from the amount of material deposited on individual targets. Initial studies with transplutonium compounds will begin in the next report period and will concentrate on the oxides and halides of these elements.

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6.2.4 Studies of Transplutonium Hydrides, Pnictides, and Chalcogenides (J. K. Gibson, R. G. Haire) Hydrides

The crystal structures and lattice volumes of the lanthanide and actinide hydrides may be used to infer the bonding valence of the metal species in these unique semimetallic compounds. Recent work on the californium

system has concluded our efforts to establish the basic phase/structural behavior of the accessible transamericium hydrides and interpret this information in terms of the actinide valence in the hydrides.

As we reported previously¹, the nature of the hydrides formed by curium² and berkelium³ clearly supports a trivalent state for the actinides therein, this in accord with the lanthanide (except Eu and Yb) and preceding actinide (Np-Am) hydride systems. Since the structural properties of their hydrides are sensitive to variations in the lanthanide/actinide valence in these compounds, it was anticipated that californium hydride(s) would be an interesting system to investigate. The fact that californium is divalent in certain compounds and that californium metal is close to being classified as a divalent metal suggested that californium may display a reduced valence state in its hydride(s) relative to preceding actinides in their hydrides.

Powder X-ray diffraction studies have been performed on several submilligram samples of californium hydrides, prepared by direct reaction of ²⁴⁹Cf metal and hydrogen at 100-200°C.⁴ A face centered cubic (fcc) pro-

duct with lattice parameter $a_0 = 0.5285(5)$ nm was obtained and is considered to be californium dihydride, CfH_{2+x} (where x is believed to be in the range $-0.2 \leq x \leq 0.3$), by analogy with lanthanide and other actinide hydride systems. Lanthanide and actinide elements which form a fcc dihydride also form a trihydride. However, a californium trihydride with hexagonal-symmetry could not be prepared even under conditions of 12 bar H_2 at 100°C. The lattice volume observed for the CfH_{2+x} products together with the inability to prepare CfH_3 , either due to the reduced stability or non-existence of this trihydride, suggests a reduced valence for Cf relative to the trivalent metal species found in other lanthanide and actinide fcc dihydrides. As seen in Figure 6.8, the CfH_{2+x} lattice volume is larger than anticipated by extrapolation from the preceding elements. This effect for CfH_{2+x} is comparable to that exhibited by fcc YbH_{2+x} (see Fig. 6.8) and might be explained similarly by considering CfH_{2+x} to be a mixed valence (Cf(II)/Cf(III)) compound.

Although several divalent and many trivalent californium compounds are known, no mixed- or intermediate-valence Cf(II-III)

Fig. 6.8. Formula volumes of lanthanide (Ln---) and actinide (An—) dihydrides ($\text{nm}^3 \times 10^3$ per MH_{2+x}): X = face centered cubic (fcc) LnH_{2+x} ; Δ = orthorhombic LnH_2 ; O = fcc AnH_{2+x} ; θ = tetragonal ThH_2 ; $\diamond$ = body centered cubic PaH_2 .

system has previously been reported. It is thus of particular interest to further clarify the nature of the Cf species in CfH_{2+x} and several studies of this compound are currently being considered. The thermodynamic stability of CfH_{2+x} may reflect a reduced Cf valence therein and hydrogen partial pressures would provide such information. The limited quantity of material available make hydride decomposition measurements difficult but preliminary work with lanthanide hydrides in a 1-300 amu mass spectrometer system suggests that Knudsen effusion measurements may be feasible in this case. In addition, magnetic studies of CfH_{2+x} are being performed in collaboration with the solid state physics group⁵ and may further clarify the nature of this compound.

Pnictides and Chalcogenides

The transplutonium mononictides offer a group of chemically similar compounds in which the An-An (An = actinide) separation may be gradually increased by substitution of pnictogens of increasing radius. Because of the critical effect of the An-An distance on 5f electron interactions/bonding, this group of compounds provides an opportunity for systematically probing effects unique to the actinide elements. Although the Am, Cm, Bk, and Cf mononictides of N, P, As, and Sb (except CfP) have previously been prepared and characterized, only the monobismuthide of americium has been similarly studied.⁶ A tentative lattice parameter suggested for fcc CmBi ($a_0 = 0.624 \text{ nm}$)⁷ is not in accord with those for the preceding actinide monobismuthides and, if correct, might imply a unique nature of curium monobismuthide. Our goal is to prepare and verify the lattice parameter of CmBi and extend these studies to BkBi and CfBi. In addition to establishing the basic crystal chemistry of these compounds, magnetic studies in collaboration with the solid state physics group⁵ could provide further characterization. Preliminary preparative and powder X-ray

diffraction studies using Gd as a stand-in for the transplutonium elements have led to the development of a microscale synthetic technique for these materials.

The behavior of the lanthanide monochalcogenides and especially the divalency of typically trivalent samarium in SmCg (Cg = S, Se, Te) render the transplutonium monochalcogenides a promising group of compounds for probing the trend towards divalency beyond Bk in the actinide series. In particular, because of the similar redox behavior of Sm and Cf, it might be expected that CfCg would contain divalent Cf, in contrast to the trivalent An species in AmCg, CmCg, and probably BkCg. Because of the small quantities of Bk and Cf available, it is impractical to prepare their AnCg compounds by direct reaction of stoichiometric quantities of the elements ($1\text{An} + 1\text{Cg}$) and only monochalcogenides through Cm have been reported. We have attempted to develop a synthetic route to lanthanide/actinide monochalcogenides on the microscale utilizing a controlled chalcogenide fugacity in $\text{H}_2/\text{H}_2\text{S}$ and $\text{H}_2/\text{H}_2\text{Se}$ mixtures in contact with the lanthanide/actinide metallic element at elevated temperatures. Using samarium for the developmental work, its sesquichalcogenides (Sm_2S_3 , Sm_2Se_3) have been prepared but the stability of these higher stoichiometry compounds has as yet prevented the preparation of the monochalcogenides by this method. The chalcogenide fugacity/activity necessary to obtain the lower stoichiometry compounds may prove too low for the $\text{H}_2/\text{H}_2\text{Cg}$ mixtures practically available to us.

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6.2.5 Spectroscopic and Electrochemical Studies of Selected Lanthanides and Actinides in Acetonitrile with Oxygen Donor Ligands¹
(G. F. Payne², J. R. Peterson³)

Spectroscopy (both in solution and in solids), cyclic voltammetry and electrochemistry have been applied to the study of the Ce(IV)/Ce(III), Pr(IV)/Pr(III), Tb(IV)/Tb(III), and the Am(IV)/Am(III) redox couples in complexing phosphine/arsine oxide acetonitrile solutions. It has been known for a number of years that oxygen donor ligands such as these can be used to stabilize tetravalent species^{3,4} and more recently^{5,6} qualitative/quantitative studies of ligand donor strength towards tetravalent uranium and thorium have been carried out. Therefore, because these ligands are known to complex the tetravalent state extremely well, experiments were carried out with selected trivalent lanthanides and actinides in the presence of such ligands in acetonitrile in an effort to oxidize them to the (IV) state. It has been found that the strong complexation provided by these ligands (especially triphenylarsine oxide (TPAsO)) greatly affects the formal reduction potentials of these redox couples favoring the formation of the higher oxidation state.

In these studies we have discovered new conditions which lower the oxidation potential of Ce(III) to Ce(IV) significantly. Ordinarily Ce(IV) is prepared in aqueous solution with oxidizing agents giving a

potential around 1.7 V.⁷ We found that just by bubbling air/oxygen through a solution of a cerium(III) salt (nitrate, perchlorate, or chloride, although the latter is only sparingly soluble in acetonitrile) in the presence of TPAsO in acetonitrile at about 70°C, Ce(III) was oxidized to Ce(IV). The cerium(IV) could be detected spectrophotometrically. With the nitrate and perchlorate the originally colorless solutions turned pale yellow in a matter of minutes. With the chloride the reaction time was a little longer (~15 minutes) but the initially colorless solution this time became bright yellow. Crystals were obtained from this latter solution, and from preliminary studies it appears the complex is a superoxide (chlorides replaced) with TPAsO co-ordinated to the metal. Ozonolysis was also attempted for the nitrate and perchlorate (chloride ion oxidized by ozone) in acetonitrile solutions in the presence of triphenylphosphine oxide (TPPO), methyldiphenylphosphine oxide (MDPPPO) and TPAsO. Not surprisingly cerium(IV) was detected in all cases. Cyclic voltammetry did not provide any useful results in these cases, since it appears that the shift in the formal potential due to complexation with these ligands is greater than 1.7 V and therefore the complex is formed before any potential is applied. Also once these tetravalent species are formed, they are extremely difficult to reduce. This latter observation could possibly be the result of steric crowding of the metal ion due to the bulky nature of these ligands.

Tetravalent praseodymium and terbium have standard (IV)/(III) potentials of about 3.2 V and 3.1 V, respectively,⁷ and therefore, can only exist in solution as complexes. They have both been stabilized in aqueous, alkali metal carbonate solutions⁸ and also as solids,^{9,10} but never in complexing non-aqueous solutions. In this work we found that by dissolving the metal nitrate and the TPAsO ligand in acetonitrile and ozonizing the solution for about 4 hrs at about 70°C,

we could detect both Pr(IV) and Tb(IV) spectrophotometrically. The known trivalent praseodymium peaks in the visible region were not observed. However, this could not be verified for terbium since the terbium(III) absorption peaks are located at wavelengths shorter than 400 nm, and these were masked by the ingrowth of a charge transfer band in the lower end of the visible region, as is typical of these tetravalent species. A cyclic voltammogram was also recorded for the praseodymium(III) nitrate - TPAsO - acetonitrile solution with LiClO_4 as the supporting electrolyte. This showed oxidation taking place at about 0.7 V, thus giving us a shift of about 2.5 V in the Pr(IV)/Pr(III) standard reduction potential. Without TPAsO in the solution a straight-line voltammogram was obtained.

Tetravalent americium has a standard (IV)/(III) potential of about 2.6 V¹¹ and is therefore unstable in most mineral acids. It is possible, however, to prepare stable Am(IV) in strongly complexing aqueous solutions such as concentrated alkali metal fluorides,¹² concentrated phosphoric acid,^{13,14} and concentrated aqueous, alkali metal carbonate solutions.¹⁵ Since we had already stabilized Ce(IV), Pr(IV), and Tb(IV) using oxygen donor ligands, it seemed reasonable to suppose we could stabilize Am(IV) under the same conditions.

Unfortunately, during the ozonolysis of the americium(III) nitrate - TPAsO - acetonitrile solution, a large quantity of the material precipitated out of solution and thus made it impossible to determine if oxidation had occurred. However, from the cerium studies we had already determined that the shift in the formal potential due to TPAsO complexing was greater than 1.7 V. Therefore, bubbling the americium(III) nitrate - TPAsO - acetonitrile solution with oxygen at $\sim 70^\circ\text{C}$ was attempted. From spectrophotometric studies based on the reduction in size of the characteristic trivalent americium peak at 510 nm and the concomitant ingrowth of a

charge transfer band, it was estimated that approximately 60% of the americium(III) had been oxidized to americium(IV). A cyclic voltammogram was recorded for the americium(III) nitrate - TPAsO - acetonitrile solution with LiNO_3 as the supporting electrolyte. This showed the formal potential of the Am(IV)/Am(III) couple in this solution to be about 0.3 V, thus, giving us a shift of about 2.3 V in the Am(IV)/Am(III) standard reduction potential. Thus there is an apparent constancy of shift for both praseodymium and americium complexed by TPAsO, similar to what was found in carbonate solution.¹⁵ A similar oxidation experiment, substituting americium(III) chloride for americium(III) nitrate was also carried out. Once again, as with cerium, the chloride is not as soluble in acetonitrile as the nitrate. Therefore, the chloride reacts much more slowly, giving a reaction time of the order of about 15 minutes. From spectrophotometric studies it was determined (based on the reduction in size of the Am(III) peak at 510 nm) that in this case we had greater than 95% oxidation of Am(III) to Am(IV) using oxygen as the oxidizing agent. A cyclic voltammogram was recorded for the chloride "solution", but the low solubility of americium(III) chloride prevented our obtaining a useful voltammogram.

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6.2.6 Magnetic Studies of Selected Lanthanide and Actinide Metals and Compounds¹
(S. E. Nave,² J. R. Moore,² P. G. Huray,² R. G. Haire, J. K. Gibson, J. R. Peterson³)
Californium Oxides

Since the 5f electronic wavefunctions are localized for transamericium actinide compounds, the near free-ion behavior allows one to determine the applicability of an intermediate-coupling model through the determination of their local paramagnetic moments. Intermediate coupling also becomes more important with increasing atomic number

so the near-ionic oxide compounds of heavy actinides provide a system through which to study this effect.

In addition, the oxide compounds are of interest for investigating crystal-field interactions. The dioxide has a face-centered-cubic structure, while the sesquioxide exists in both a body-centered-cubic form and a monoclinic form for oxides beyond americium. The reversible change in going from the dioxide to the bcc sesquioxide involves a change in oxidation state and coordination number but preserves a cubic symmetry, while the irreversible change from the bcc to monoclinic sesquioxide preserves oxidation state but involves a change in symmetry and coordination number.

Magnetic susceptibility measurements have been completed on the oxide system of californium. Polycrystalline samples of Cf_2O_3 (in both the cubic and monoclinic crystal structures), Cf_7O_{12} , CfO_2 , and BaCfO_3 have been studied in magnetic fields of up to 50 kilogauss and at temperatures between 4.2 and 340 kelvin. All of the oxides exhibit Curie-Weiss behavior at temperatures above about 100 kelvin and show indications of anti-ferromagnetic ordering at temperatures below 20 kelvin. Crystal field effects are apparent at intermediate temperatures.

The measured values for the effective paramagnetic moments (μ_{eff}), Weiss paramagnetic temperatures (θ_p) and anti-ferromagnetic transition temperatures (T_N) for the oxides are summarized in Table 6.3. The variation in μ_{eff} as the stoichiometry changes from CfO_2 to Cf_2O_3 is consistent with the change in the charge state of the californium from 4+ to 3+. The measured values compare well with theoretical values based on an intermediate coupling model of the californium electronic structure.

Investigating Mechanisms for Magnetic Ordering in Actinide Elements

Like their lanthanide homologues, the transplutonium actinide metals and

Table 6.3. Magnetic Results for Californium Oxide Compounds

		ν_{eff} (ν_{g})	ν_{eff} (intermediate coupling) (theory)	θ_{p} (kelvin)	T_{N} (kelvin)
CfO_2	fcc	$9.1 \pm .2$	9.3	70 ± 10	19 ± 1.5
$\text{Cf}_{12}\text{O}_{12}$	rhombohedral	$9.5 \pm .2$	9.7	95 ± 15	8 ± 2
Cf_2O_3	monoclinic	$10.1 \pm .2$	10.2	80 ± 15	8 ± 2
	bcc	$9.8 \pm .2$	10.2	115 ± 15	19 ± 1.5
BaCfO_3	perovskite-type	$9.2 \pm .2$	9.3	210 ± 20	7 ± 2

semimetallic compounds have a rich variety of types of magnetic ordering at low temperatures. There are three types of mechanisms considered as responsible for magnetic interactions between near neighbor actinides in these materials. The local actinide moments can be coupled by: (1) direct overlap of actinide wavefunctions (direct exchange); (2) overlap of two actinide wavefunctions with that of a common anion (super exchange); or (3) perturbation of the spin density of the conduction electrons by the local moment of one actinide core which then extends far enough to interact with a second actinide local moment (Ruderman-Kittel-Kasuya-Yosida or RKKY interaction). Magnetic measurements allow a determination of transition temperatures and in some cases the type of magnetic ordering. Thus the measurements provide useful parameters for studying the interaction mechanisms. Binary compounds of an actinide and a pnictogen (Group VA element) form an interesting group of compounds for studying these interactions. They are semimetallic and thus have partially populated conduction bands - making RKKY interactions possible. In addition, the actinide-actinide spacing increases with heavier pnictogen providing a way to probe the separation dependence of the 3 types of interaction.

Measurements have been previously reported on curium and berkelium pnictides^{4,5} and

during this period have been extended to the californium pnictides CfN , CfAs , and CfSb . The results of these measurements are summarized in Fig. 6.9 where the ordering temperatures are plotted versus actinide-actinide separation. In the same figure, results for lanthanide homologues and light actinide pnictides are given for comparison. It appears the curium pnictides are more like the light actinides since they exhibit high transition temperatures; while the californium pnictides are more like their lanthanide homologues, the dysprosium pnictides. This may indicate less direct exchange or superexchange due to increasing localization of the 5f wavefunction. The berkelium nitride transition temperature is intermediate to that of CmN and CfN but the remainder of the berkelium pnictide group must be measured to confirm any generalization.

The hydrides of selected transplutonium actinides have also been studied during this period. They form another system for studying these interaction mechanisms by virtue of the fact that they are similar to metals with electrons removed or added to the conduction band depending on the degree of hydriding. Clearly the strength of the RKKY interaction should be dependent on the number of conduction electrons, i.e., a decrease in conduction electrons should lower the transition temperature. Measurements on CfH_x

Fig. 6.9. Ordering temperature (K) versus actinide-actinide or lanthanide-lanthanide spacing (Å) for mononitrides as indicated. $\square T_M$ $\bullet T_C$

(where x is near 2) indicated that it has a lower transition temperature than the metal, as expected. Preliminary measurements on curium hydrides have been complicated by presence of oxide or metallic phases as impurities.

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6.2.7 Structural Chemistry of Solid Solutions of Lanthanide Titanates

(C. E. Bamberger, G. M. Begun, H. W. Dunn¹)

In continuing systematic studies of the formation of solid solutions between titanates of "light" and "heavy" lanthanide elements and of lanthanide elements and bismuth the following systems were examined by x-ray diffraction (XRD) and Raman spectroscopy: $x\text{Ln}_2\text{O}_3 \cdot (2-x)\text{Bi}_2\text{O}_3 \cdot 3\text{TiO}_2$ (I) and $x\text{Ln}_2\text{O}_3 \cdot (1-x)\text{Bi}_2\text{O}_3 \cdot 4\text{TiO}_2$ (II). The study of system (I) led us to review the bibliography and investigate experimentally the system

$\text{Ln}_2\text{O}_3\text{-Ln}_2\text{Ti}_2\text{O}_7$ to ascertain whether or not species with stoichiometry $\text{Ln}_4\text{Ti}_3\text{O}_{12}$ exist for all the lanthanide elements. It was found that Dy, Ho, Y, Yb, and Lu formed a pyrochlore-type phase with that stoichiometry; this structure changed to a fluorite-type phase by dissolution of additional Ln_2O_3 . During the course of the experiments the Raman spectra of hexagonal Dy_2TiO_5 , orthorhombic Gd_2TiO_5 and of fluorite Yb_2TiO_5 were also recorded. Despite the fact that not all the lanthanide elements appear to form the line compound $\text{Ln}_4\text{Ti}_3\text{O}_{12}$, all dissolve to some extent into orthorhombic $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. The maximum solubilities of the lanthanide elements were determined to be dependent on their ionic radii, the larger ones being more soluble.

The study of system (II) revealed that all the lanthanide elements and scandium form solid solutions with $\text{Bi}_2\text{Ti}_4\text{O}_{11}$. The extent of the dissolution can be correlated with the ionic radii of the guest elements; however, opposite to what was observed with system (I), in (II) the solubility increases as the ionic radius decreases. It was also found that the solid solutions are metastable with respect to temperature. Because their decomposition at

1000°C as a function of time was readily ascertained with Raman spectroscopy by the appearance of rutile in the spectra, we speculated that the isothermal decomposition of the solid solutions may also take place at lower temperatures.

Some preparations of $n\text{TiO}_2 + \text{Bi}_2\text{O}_3$ made to be used as Raman spectral standards with $4 < n < 5.5$ showed only the presence of $\text{Bi}_2\text{Ti}_4\text{O}_{11}$ when examined by XRD or Raman spectroscopy. In order to determine whether this was due to the formation of $\text{TiO}_2\text{-Bi}_2\text{Ti}_4\text{O}_{11}$ solid solutions or lack of sensitivity to detect TiO_2 by the analytical methods used, the system $\text{TiO}_2\text{-Bi}_2\text{O}_3$ was studied systematically at 900° and 1050°C. It was found that for $n > 5.5$ XRD was able to detect TiO_2 and Raman spectroscopy for $n > 6.5$. Measurements of Raman peak widths and of areas of selected peaks led us to conclude that TiO_2 does not dissolve in $\text{Bi}_2\text{Ti}_4\text{O}_{11}$. It was additionally found that mechanical grinding of the commonly obtained "high temperature" form of $\text{Bi}_2\text{Ti}_4\text{O}_{11}$ converts it to the "low temperature" form.

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7. SEPARATIONS CHEMISTRY

This research employs a multifaceted approach to understanding the fundamental role of molecular structure and bonding in determining the chemical selectivity and physical properties of solvent-extraction and related separation systems. Systematic studies of synergistic combinations of crown ethers and organophilic acids as extractants for alkali, alkaline earth, and transition metal cations (7.1.2, 7.1.3) are followed by detailed analyses of the more promising systems. Systematic studies are also being made of polymer-supported organophosphorus extractants (7.1.4, 7.1.5). The detailed analyses are designed to ascertain as much as possible about the thermodynamics of the reactions and the structures of the participants in them. The techniques used include computer-assisted analysis (7.2.1) of extraction equilibrium measurements (7.2.3, 7.2.6, 7.2.7) and of osmometry (7.2.2) to identify the species formed in the organic phase. FT infrared, Raman, and NMR spectral measurements (7.2.4, 7.2.5) are made to determine the nature of their bonding and to correlate their structure with that of solids determined by X-ray diffraction of single crystals (7.3). Finally, efforts are underway to synthesize extractant molecules (7.4) which will exploit those principles of extraction which are evolving in this work.

7.1 Systematic Studies

In these studies, tests are performed either to survey the extraction of a given metal cation by a series of related reagents, or to survey the extraction of a series of related cations by one extractant of selected type and structure. Currently, our attention is focused primarily on extractants that are synergistic combinations of crown ethers and organophilic acids. The results of such systematic studies, while insufficient to give details about the mechanism of the separations, do enable one to make fairly reliable predictions about the solubility and phase distribution characteristics of a proposed separations agent, about the kind of ions it will extract or absorb, and about how to change its structure and the extraction conditions to obtain a desired separation. If only one kind of information could be obtained in separations chemistry studies, then the results of systematic tests such as these would be the most useful for developing novel separation systems. In fact, such results form the basis upon which more detailed studies may be formulated and a proper understanding of mechanisms may be achieved.

7.1.1 Solubility and Phase Distribution of Solvent Extraction Reagents

(W. J. McDowell, G. N. Case)

Two acyclic polyether dicarboxylic acids prepared by R. A. Bartsch and B. P. Czech at Texas Tech University were examined for distribution to aqueous phases from organic solution. The two compounds were, bis-1,8-(2'-carboxy-3-naphthoxy)-3,6 dioxooctane, 1 (chloroform soluble) and bis-1,8-(2'-carboxy-4'-decyl(phenoxy))-3,6 dioxooctane, 2 (toluene soluble). A solution of 1.6 M 2 could be made in toluene and 0.07 M 1 could be made in chloroform. Distribution of the acid form of these compounds to water from a 0.05 M solution in the above solvents was small (< 1%). The alkali metal salts are completely aqueous soluble at low ionic strength. With an aqueous phase 4 M in the alkali metal chloride about 60% of each compound distributed to the aqueous phase as the alkali metal salt. At an ionic strength of 1 M, precipitation of lithium and sodium salts were observed in both phases. Tests for precipitation of other alkali metal salts were not made.

Examinations of these compounds for solvent extraction of strontium, barium, and radium were described last year.¹ A paper describing the separation of barium and radium by 1 was submitted to Solvent Extraction and Ion Exchange for publication.

1. W. J. McDowell and G. N. Case, Chem. Div. Annu. Prog. Rep. Jan. 31, 1985, ORNL-6152 (May 1985), p. 97.

7.1.2 Synergistic Extraction with Crown Ethers and Didodecyl-naphthalene Sulfonic Acid (HDDNS): Alkalies, Alkaline Earths, and Selectivity Reversals

(W. J. McDowell, B. A. Moyer, G. N. Case, F. I. Case)

Studies of the extraction of alkali, alkaline earth and first-row transition elements by mixed solutions of didodecyl-naphthalene sulfonic acid (HDDNS), 0.1 M, and one of the macrocycles, 0.05 M in toluene were reported in the last annual report.¹ A paper entitled, "Selectivity in Solvent Extraction of Metal Ions by Organic Cation Exchangers Synergized by Macrocycles: Factors Relating to Size and Structure" on this and additional work has been accepted for publication by Solvent Extraction and Ion Exchange. The abstract follows:

Crown ethers and related macrocycles strongly synergize the extraction (phase transfer) of certain metal ions from aqueous nitrate solutions to toluene solutions of organophilic sulfonic,

phosphoric, and carboxylic acids. For alkali metals, the degree of synergism is related to the size correspondence between the macrocycle cavity and the metal ion if macrocycles of similar type and substitution are considered. Alkaline earth metals are similarly strongly synergized but the size-correspondence relationship is less pronounced. Other factors seem to affect selectivity of these elements. Tert.-butylbenzo-substituted crown ethers of the same size are much less effective synergists for the alkaline earths than cyclohexano- or tert.-butylcyclohexano-substituted compounds. However, with synergism in alkali metal extraction, the reverse is generally true; that is, tert.-butylbenzo-substituted crown ethers are better synergists than cyclohexano-substituted crown ethers. Effects involving the electron-withdrawing influence of the aromatic substituents and the flexibility of the ring may explain this selectivity reversal. The extraction of the divalent first-row transition metals, iron, cobalt, and nickel, is not synergized by any of the macrocycles. However, manganese and zinc with half and completely filled d-shells are synergized suggesting a possible correlation of synergistic coordination effects with ligand field stabilization in the first-row transition elements. Studies to determine the stoichiometry of the organic-phase complexes indicate a single crown ether associated with each molecule of the metal salt of the organic-phase acid. In some cases neutral organic acid molecules may also be associated with the complex.

In continued extraction tests from acid nitrate systems, a quantity of HDDNS purified by a procedure developed for dinonylnaphthalene sulfonic acid² has been used. The macrocycles currently in use are listed in Table 7.1.

Table 7.1. Macrocycles in current use

Macrocycle name	Acronym	Cavity diameter (Å)
octamethylperhydrocyclotetra-furfurylene	OMPCTF	1.2 - 1.5
benzo-14-crown-4	B14C4	1.2 - 1.5
<u>tert.</u> -butylcyclohexano-15-crown-5	tBC15C5	1.7 - 2.2
<u>tert.</u> -butylbenzo-15-crown-5	tBB15C5	1.7 - 2.2
dicyclohexano-18-crown-6	DC18C6	2.7 - 2.9
di(<u>tert.</u> -butylcyclohexano)-18-crown-6	D(tBC)18C6	2.7 - 2.9
di(<u>tert.</u> -butylbenzo)-18-crown-6	D(tBB)18C6	2.7 - 2.9
dicyclohexano-21-crown-7	DC21C7	3.4 - 4.3

Repetitions of the experiments that had previously been done with impure material (thought to contain unsulfonated didodecyl-naphthalene) gave results identical to that obtained with the impure HDOHS. Some extraction tests were also repeated with amounts of the nonradioactive test ion (0.001 to 0.0001 M) added in addition to the radionuclide (usually $<10^{-8}$) to check for possible small concentrations of any impurity in the system that might be a better extractant than the compounds of interest. These tests also gave results identical to the original ones.

The data with purified HDOHS confirmed that there is only one crown ether complexed with each metal, but indicates that the sulfonic acid reagent dependence is complicated by aggregation and by interaction of the sulfonic acid with the macrocycle (see Sect. 7.2.2).

The reversal of the selectivity of the synergistic effect of the 18C6 ring by changing the substituents from cyclohexano to benzo has been reported previously.³ The cyclohexano-substituted ring synergizes strontium and barium extraction more strongly than does the *tert.*-butylbenzo-substituted ring while the benzo-substituted ring synergizes potassium, rubidium, and cesium more strongly. Investigation of this and related phenomena are continuing. Selectivity reversals noted to date are listed in Table 7.2.

The same pattern of selectivity is seen between rubidium and barium and cesium and barium using di(*tert.*-butylbenzo)-18-crown-6 (D(tBB)18C6) and dicyclohexano-18-crown-6 (DC18C6). However, in sodium extraction synergized by the 15-crown-5 ring a small increase in synergism ($D = 9$ to $D = 15$) occurs when *tert.*-butylcyclohexano-15-crown-5 (tBC15C5) is substituted for *tert.*-butylbenzo-15-crown-5 (tBB15C5).

In the 18-crown-6 compounds, inductive effects from the benzo-substitution would be expected to reduce the electronegativity (basicity) of four of the six oxygens. This would explain a reduction of synergism (bonding strength) as in the case of the alka-

Table 7.2. Selectivity reversal due to macrocycle substituents
For 0.1 M HDOHS, 0.05 M Crown Ether
0.2 M Aqueous HTrTc Acid

Element	Synergist	D_M
K	D(tBB)18C6	350
	D(tBC)18C6	46
Rb	D(tBB)18C6	70
	DC18C6	16
Cs	D(tBB)18C6	30
	DC18C6	3.8
Sr	D(tBB)18C6	300
	D(tBC)18C6	6,000
Ba	D(tBB)18C6	1,000
	DC18C6	6,000

line earths (and of sodium) but not an increase as in the case of potassium, rubidium, and cesium. Relative size seems to have little to do with this reversal phenomenon. Using the ionic radii of Shannon and Prewitt,⁴ strontium is smaller than the 18C6 cavity ($d = 2.50$ for Sr, 2.68 to 3.86 for 18C6) while barium is within the range ($d = 2.84$). Rubidium ($d = 3.20$) and cesium ($d = 3.56$) are both larger than the 18C6 cavity. These systems have not been completely characterized (equilibrium-analyses, spectroscopic, and osmometric experiments in progress), so we are not sure of the stoichiometry of extracted species in all cases. However, the evidence available at present suggests that only a single crown ether is associated with each metal. Thus differences in stoichiometry do not appear to be a likely reason for the reversals shown in Table 7.2. The difference in the ring flexibility of the two crown ethers, D(tBB)18C6 and D(tBC)18C6, may offer the best possibility of explaining these reversals. The cyclohexo-substituted crown ether is more flexible,⁵ and although both the alkali and alkaline earth ions are spherically symmetrical, perhaps the higher charge density of the alkaline earth ions attempt to pull the

crown ether ring into some configuration that is readily attained only by this more flexible ring. At the same time, the less flexible, benzo-substituted ring might favor ions in which a reduction in entropy requirements is the important factor. That is, sodium, potassium, rubidium and cesium, having lower charge density than the alkaline earths, might profit more in overall reaction energy from a structure that requires less rearrangement to provide a cavity into which the metal ion could fit. If we exclude sodium, this idea is consistent with the preference of the alkali metals for the more rigid macrocycle.

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3. W. J. McDowell, G. N. Case, and F. I. Case, Chem. Div. Annu. Prog. Rep. Jan. 31, 1985, ORNL-6152 (May 1985), p. 95.
4. R. D. Shannon and C. T. Prewitt, Acta Cryst. A25, 925-946 (1969).
5. W. Wallace, C. Chen, E. M. Eyring, and S. Petruscci, J. Phys. Chem. 89, 1359 (1985).

7.1.3 Synergistic Extraction with Crown Ethers and Didodecylinaphthalene Sulfonic Acid: First-Row Transition Elements

(W. J. McDowell, B. A. Moyer, G. N. Case, F. I. Case)

The effects of the macrocyclic ethers on the extraction of divalent manganese, iron, cobalt, nickel, copper, and zinc by HDDNS have been reported previously.¹ Only manganese and zinc were shown to be synergized to any significant extent and only by the 15C5 ring, the size expected to fit these ions. Distribution coefficients for iron, cobalt, nickel, and copper are depressed by the presence of most of the macrocyclic ethers. Such depression of the distribution coefficient can be explained

by assuming a competing reaction between the crown ether and the HDDNS. Confirmation of such a competing reaction has been provided by vapor-phase osmometry and by the observation that the addition of macrocycles to the amber colored HDDNS solutions (either as-received or purified) causes bleaching in various amounts depending on the macrocycle.

Judging from the differences in the effectiveness (or lack of effectiveness) of tBC15C5 as a synergist across the divalent first-row transition metal series in Fig. 7.1, significant differences in the coordination of tBC15C5 to the various metals may be inferred. We find the strongest synergism in the case of manganese and zinc in which the d-electron levels are half-filled and filled, respectively. Both of these d-electron configurations are spherically symmetrical giving no ligand-field stabilization effect in bond formation. Manganese and zinc consequently are expected to behave chemically more like the alkaline earth elements than their neighbors in the first row of the periodic table, and this is evidenced by the synergistic effects produced by the crown ether tBC15C5.

The weak or nonexistent ability of tBC15C5 to synergize the extraction of divalent iron,

Fig. 7.1. Variation of the synergistic factor (HDDNS + tBC15C5) across the first-row transition elements.

cobalt, nickel, and copper relative to manganese and zinc suggests that ligand field stabilization energy (LFSE) may correlate with selectivity in macrocycle-synergized extraction of transition metals. The apparent ability of tBC15C5 to coordinate the divalent first-row transition metals follows the order $Mn^{2+} > Fe^{2+} \approx Co^{2+} \approx Ni^{2+} < Cu^{2+} < Zn^{2+}$ (see Fig. 7.1). This unusual order suggests that the extraction and accompanying complexation of the elements iron to copper leads to a decrease in LFSE rather than the commonly observed increase.²⁻⁵ Such a decrease in LFSE may be rationalized from the weak-field nature of ether donors and from the inability of the 5-membered macrocycle to accommodate a pseudo-octahedral geometry. Since the manganese and zinc undergo zero change in LFSE in complex formation, they will gain a selectivity advantage over Fe^{2+} to Cu^{2+} as is indicated in discussion of the origin of the Irving-Williams order³ or its inverse.⁴

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7.1.4 Application of Dual Mechanism Bifunctional Polymers to Metal Ion Recovery

(S. D. Alexandratos,¹ P. T. Kaiser,¹ A. J. Walder,¹ W. J. McDowell)

A new bifunctional polymer-supported extractant for use in metal ion recovery has been synthesized incorporating primary phosphinic acid/secondary phosphine oxide, as well as primary and secondary phosphinic acid ligands, depending on the method of syntheses (see Fig. 7.2). The principal functionalization reaction occurs on polystyrene beads with PCl_3 followed by hydrolysis. These bifunctional polymers operate by a dual mechanism in that they will ion-exchange with a given metal at low pH and then reduce it to its zerovalent state if it has an appropriate reduction potential (see Fig. 7.3). The concept of dual mechanism bifunctional polymers is thus advanced to describe phosphinic acid resins and their derivatives. The reducing agent is the primary phosphinic acid ligand (and the secondary phosphine oxide ligand, if present). Extraction studies with zinc, mercury and silver have been carried out. Comparative studies with phosphonic acid, sulfonic acid, and carboxylic acid resins clearly indicate the mechanism of action as well as an extraordinarily high affinity for the transition metal ions by the phosphinic resins. For example, using 1 milliequivalent of resin and 5 mL of aqueous phase with the 1 milliequivalent of test ion, in the presence of excess sodium ions, the phosphinic resins absorb 70%

X = H WITH NEUTRAL AQUEOUS HYDROLYSIS. X = OH WITH BASE HYDROLYSIS.

Fig 7.2. Reactions for forming bifunctional resins.

Fig. 7.3. Reduction of metal ion by resin.

of the mercury (II) from the solution as opposed to 25% absorbed by sulfonic acid resins. The phosphinic resins reduce all of the mercury absorbed until all of the primary sites at which ion exchange occurs are oxidized.

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7.1.5 Lanthanide and Actinide Extraction by Polymer-Supported Extractants

(S. D. Alexandratos,¹ D. R. Quillen,¹ M. J. McDowell)

The extracting ability of phosphinic acid resins for europium, thorium, uranium, americium, and plutonium was examined as a function of acid concentration from nitric acid solutions both at varying and constant ionic strength. The phosphinic resins show better extraction for these ions than sulfonic acid resins, especially from high acid solution (4 M HNO₃) due to the superior coordination ability of the phosphoryl oxygen. With conditions as described in Sect. 7.1.4, except that the test ions were present in tracer level, these resins absorbed 83% Eu, 83% Am,

97% UO₂, and 86% Pu compared to 70% Eu, 70% Am, 71% UO₂, 77% Pu for a sulfonic acid resin. The phosphinic resins are also superior in the presence of excess sodium. From a solution of 0.2 M HNO₃/3.8 M NaNO₃, the phosphinic resin absorbs > 99% of the above ions vs 66% Eu and Am, 77% UO₂, and 53% Pu for the sulfonic acid resin.

Our current studies also involve what may be the first example of a polymer-supported synergistic extraction system. A new resin containing both phosphinic acid and phosphonate ester groups has been synthesized (see Fig. 7.4). The extraction of americium by this resin with varying acid/ester ratio has been studied. The highest distribution coefficient is obtained at a ratio acid/ester of 1.

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7.2 Detailed Studies of Extraction Systems

Systems that show promise as separations processes or stand as representative of a class of extractants are examined in greater detail by a variety of measurements. The

Fig. 7.4. Preparation of a polymer-supported synergistic extraction system.

degree of association of aggregation in solution is usually measured using vapor phase osmometry (VPO). The dependence of the distribution coefficient on extractant, synergist, aqueous acid concentrations, and sometimes, on aqueous anion concentration is studied in detail. These data are analyzed by fitting to appropriate equilibrium expressions, graphically if feasible, or by computer least-squares methods if not; the object being to define the organic phase species and write the reactions involved. Following this, nuclear magnetic resonance, infrared, and Raman spectral measurements are made to obtain information related to bonding in the organic-phase compounds.

7.2.1 The Interpretation of Equilibrium Data from Synergistic Solvent Extraction Systems

(C. F. Baes, Jr., W. J. McDowell)

It is not a trivial task to determine the species formed in the organic phase of a synergistic solvent extraction system. In such solutions, the acidic extractant (HA) can be associated, the neutral organic ligand (B) can interact directly with HA, and often more than one complex of the extracted metal ion (M^{i+}) and perhaps an anion (X^{j-}) is formed. Thus there are likely to be at least five different species in the organic phase, and quite possibly several more.

The general formula for an extraction complex in such a system may be written

and the reaction for its formation may be written

If only one extraction complex is formed in appreciable amounts and all activity coefficients are assumed to be unity, then the

extraction coefficient of the metal M should be given by

$$D = K [M^{i+}]^m [X^{j-}]^x [(HA)_y]^a / y [B_z]^b / z [H^+]^{xj-mi}, \quad (2)$$

where K is the equilibrium constant for the above reaction (Table 7.3). The powers of the concentration terms may be determined from the slopes of appropriate log-log plots of D vs the concentration of each reactant, varied one at a time. Deduction of the formula or the extraction complex from these slopes, however, may require an independent knowledge of the degree of association of HA and B.

The analysis of the data by graphical means becomes rapidly more difficult and less reliable as additional species are formed. Thus there may be more than one species of HA, or there may be an additional extraction complex of M formed. These complications will lead to curved log-log plots of D vs various reactant concentrations.

Perhaps the most common complication in synergistic systems is the formation of a complex between HA and B

Table 7.3. The effect of various possible states of aggregation (RA and RB) of synergistic extractants HA and B

$$K = \frac{[M_m A_a B_b X_x H(a+xj-mi)]}{[M^{i+}]^m [X^{j-}]^x [RA]^a [RB]^b [H^+]^{xj-mi}}^*$$

State of aggregation		Coefficients	
RA	RB	ca	cb
HA	B	a	b
(HA) _y	B _z	a/y	b/z
(HA) _y	A _c H _c B _d	(a-bc/d)/y	b/d
A _c H _c B _d	B _z	a/c	(b-ad/c)/z

*The equilibrium constant for the formation of an extraction complex of a cation M^{i+} and an anion X^{j-} by synergistic extractants HA and B in various forms.

usually through hydrogen bonding. The possible consequences of such a reaction may be most easily appreciated by assuming that such a reaction consumes either HA or B completely. Then two different extraction reactions are possible, depending on which extractant is present in excess, and the formation of a given species thus shows two sets of dependencies on the concentrations of HA and B present (Table 7.3). Still, if just one complex were formed by complete reaction of HA and B, it would be possible to interpret sufficiently extensive extraction data by graphical means. In fact, of course, such a situation is not very likely and the coefficients listed in Table 7.3 reflect limiting behavior that can be used only as a guide for the choice of species with which to fit the data.

The quantitative interpretation of equilibrium extraction data requires a computer-based general least squares treatment. We have developed such a procedure using a slightly modified version of the ORGLS program of Busing and Levy.¹ We have written a set of subroutines that permits testing of a scheme of species, specified either interactively or from a data set. For each scheme the integers y , z , i , and j in Eq. (1) are specified, thus defining the reactants $(HA)_y$, B_z , M^{i+} , and X^{j+} . Each species is defined by a set of integers m , a , b , x , and w (any of which may be zero), and a preliminary value is given of the equilibrium constant for its formation reaction. Successive refinement cycles are carried out to fit the data by adjustment of the formation constants.

Similar sets of subroutines have been prepared to fit a given scheme of species to observed vapor pressures, water contents, and heats of mixing of organic solutions involved in synergistic systems. With such a variety of measurements, it should be possible to characterize fairly complicated such systems unambiguously by this sort of equilibrium analysis.

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7.2.2 Aggregation of Didodecyl-naphthalene Sulfonic Acid and Its Interaction with Crown Ethers in Toluene and CCl₄

(W. J. McDowell, S. A. Bryan,¹
R. B. Chadwick,² G. M. Case)

A number of observations related to our use of didodecyl-naphthalene sulfonic acid (HDDNS) as an extractant, both alone and in combination with macrocyclic synergists, suggests both that it is self-associated (aggregated) and that it forms intermolecular compounds with the macrocycles. Log D vs log $[HDDNS]$ curves were linear only over short regions. Further, the antagonistic effect produced by the macrocycles on the extraction of some ions could only be explained by the formation of a compound between the macrocycle and HDDNS. For quantitative interpretation of the mixed macrocycle HDDNS extraction data it was necessary to further understand both the HDDNS aggregation and its interaction with macrocycles.

Vapor phase osmometric (VPO) measurements of HDDNS in CCl₄ show the acid to be an aggregate averaging approximately 10 monomers in the concentration range 6×10^{-3} F to 1.1×10^{-2} F (gram formula weights per liter) and proton nuclear magnetic resonance (NMR) measurements (Sect. 7.2.6) suggest that aggregate is a water-containing micelle. The salt of $Sr(DDNS)_2$ in CCl₄ was also found to be an aggregate of 6 molecules over the concentration range 3.6×10^{-3} to 3.6×10^{-2} F by VPO measurements. This is in agreement with aggregation numbers found for the zinc salts of dinonylnaphthalene sulfonic acid.³ HDDNS solutions in toluene show aggregates of between 7 and 10 monomers at 0.1 F.

In more detailed studies, tBB15C5, tBC15C5 and DC18C6 mixtures with HDDNS in toluene were examined by VPO methods for evidence of inter-

molecular compound formation. In each case, the macrocycle and HDONS were mixed in various mole ratios, keeping the total moles present at 0.1 F. The continuous variation curves thus produced indicated intermolecular compound formation with the strength of the interaction increasing in the order the crown ethers are listed above. The data for tBC15C5 were mathematically fitted using the computer program described in Sect. 7.2.1 and the predominant species found together with its formation constant are listed in Sect. 7.2.3. Evidence was also obtained for intermolecular compound formation between HDONS and OC18C6 in CCl_4 by infrared methods (see Sect. 7.2.6).

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3. S. Kaufman and C. R. Singletary, J.
Colloid Sci. 10, 139-150 (1955).

7.2.3 Manganese Extraction by Didodecylinaphthalene Sulfonic Acid and Substituted 15-crown-5

(R. B. Chadwick,¹ W. J. McDowell,
C. F. Baes, Jr.)

In section 7.1.3, above, the extraction of manganese is shown to be synergized by tert.-butylcyclohexano-15-crown-5 (tBC15C5). Graphical interpretation of the dependence of the manganese distribution coefficient on tBB15C5 concentration indicates that the benzo compound does not interact with manganese. Similar graphical interpretation of manganese loading curves ($\log [M]_{\text{org.}}$ vs $\log [M]_{\text{aq.}}$) for the sulfonic acid mixed with each of the crown ethers indicated that the organic-phase manganese complexes are monomeric in manganese. Using the fitting programs described in section 7.2.1, the dependence of the manganese distribution coefficient on HDONS (HA) in the presence of constant tBC15C5 (B) and on the concentration of (B) in the presence of constant HA indicates the formation of a compound $\text{MnA}_2 \cdot 3 \cdot 4\text{HA}$. When HDONS alone (or with

tBB15C5) is used to extract manganese the organic-phase manganese species appears to be the aggregate $\text{MnA}_2 \cdot 9\text{HA}$.

Vapor-phase osmometry measurements indicate the sulfonic acid alone is associated into aggregates averaging 10 monomers and that the crown ether interacts with the sulfonic acid in solution causing the aggregates to break up.

A summary of the predominant reactions on mixing tBC15C5 (B) and HDONS (HA) in toluene, and on extraction of manganese by the two systems, HA alone and HA plus tBC15C5, and their provisional equilibrium constants (activity coefficients not included) as obtained by fitting with the computer programs described in Sect. 7.2.1 are given below:

$$\log K = 1.86$$

$$\log K = 0.57$$

$$\log K = -3.66$$

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7.2.4 Infrared, Raman, and NMR Spectral Studies of Crown Ether Complexes of Strontium and Sulfonic or Carboxylic Acids

(S. A. Bryan,¹ W. J. McDowell)

The degree of self aggregation and nature of bonding with metals of some of the acidic extractants and macrocyclic compounds has been

studied by infrared, Raman, and proton NMR spectra. Proton NMR of a 0.1 M solution of didodecyl naphthalene sulfonic acid (HDDNS) in wet carbon tetrachloride shows many bands due to naphthalene and alkyl side chains but a single band due to acidic and H_2O protons can be identified at 7.15 ppm vs tetramethylsilane (TMS). By integration of this band, the number of waters per sulfonic acid group was found to be eight. Thus, the total number of waters per 10-fold HDDNS aggregate (see Section 7.2.2) is approximately 80. It is reasonable to assume that the water molecules are hydrogen-bonded to the polar ends of the acid and that they bridge adjacent acid groups together forming an "inverted" micelle. This concept is further supported by the fact that the proton NMR band is at a low field compared to free water in carbon tetrachloride at 1.1 ppm vs TMS. By similar arguments, a micellar structure for the salt $\text{Sr}(\text{DDNS})_2$ dissolved in wet carbon tetrachloride is suggested by the downfield position of the water peak at 4.76 ppm vs TMS. Integration of this band gives the number of waters per strontium unit as ca. 11. Vapor phase osmometric (VPO) measurements of the $\text{Sr}(\text{DDNS})_2$ solutions indicate an aggregation number of six and thus lead to the

conclusion that the overall stoichiometry of the strontium sulfonate species in solution in carbon tetrachloride is $[\text{Sr}(\text{DDNS})_2 \cdot 11\text{H}_2\text{O}]_6$.

Vapor pressure osmometric (VPO) measurements of dicyclohexano-18-crown-6 (DC18C6) in water-saturated carbon tetrachloride indicate the compound to be a monomer at concentrations less than 0.1 M. The IR spectrum of DC18C6 in carbon tetrachloride shows several strong bands attributed to the carbon-oxygen stretching in the crown ether ring (see Table 7.4). The strongest of these is at 1105 cm^{-1} . Addition of HDDNS or metal DDNS salts to carbon tetrachloride solutions of DC18C6 causes the ether bands to move, as expected, to a lower frequency (Table 7.4). In the case of $\text{DC18C6} + \text{Sr}(\text{DDNS})_2$, these band shifts are believed to be due to a strong interaction of the strontium with the ether oxygens. In the case of the reaction of DC18C6 with HDDNS, the observed shift is taken (on the basis of previous studies with similar systems^{2,3}) to be due to the interaction of H_3O^+ with the ether oxygens.

Using, as an indicator, the absorbance of the ether band at 1080 cm^{-1} (for ether bonded to HDDNS), a continuous variation experiment using a mixture of DC18C6 and HDDNS in carbon

Table 7.4. Infrared band positions for DC18C6 and DC18C6 adducts in the ether region

Complexes	Ether C-O bands (cm^{-1})	
DC18C6 (uncomplexed)	1125(s)	1105(s)
$\text{Sr}(\text{DC18C6})\text{Cl}_2$	1090(s)	1073(s)
$\text{Sr}(\text{DC18C6})(\text{NO}_3)_2$	1084(s)	1075(s)
$\text{Sr}(\text{DC18C6})(\text{pivalate})_2$	1088(s,b)	
$\text{Sr}(\text{DC18C6})(\text{versatate } 1519)_2$	1091(s)	1062(sh)
$\text{Sr}(\text{DC18C6})(\text{DDNS})_2$	1093(s)	1048(s)
$\text{DC18C6} \cdot 2\text{HDDNS}$	1080(m)	

s = strong; m = medium; sh = shoulder; b = broad

tetrachloride at a constant total concentration of 0.1 M was performed. This produced a plot with a maximum at 0.33 mole fraction of DC18C6, consistent with the formation of the complex DC18C6-2HDDNS. A similar continuous variation plot obtained from mixing DC18C6 and Sr(DONS)₂ in carbon tetrachloride, using either the crown ether band at 1084 cm⁻¹ or the sulfonate band at 1466 cm⁻¹, showed a maximum at mole fraction = 0.5. This indicates that a 1:1 complex was formed between DC18C6 and Sr(DONS)₂. VPO results show this complex to be a monomer. Integration of the proton NMR peak at 3 ppm vs TMS indicates two waters per strontium complex unit. From the above VPO, NMR, and IR data, the strontium sulfonate complex with DC18C6 is the monomeric species Sr(DC18C6)(DONS)₂·2H₂O. As shown by a continuous variation experiment monitoring absorbance changes in the infrared spectra, this complex appears to form a 1:1 association with additional HDDNS. This observation is significant because an excess of HDDNS is expected to be present under most extraction conditions.

Raman spectra have been used in an attempt to determine whether the complexed strontium is located in the DC18C6 crown ether ring or not. DC18C6 complexed with SrCl₂, Sr(NO₃)₂,

Sr(pivalate)₂, and Sr(versate)₂ (the salt of a neocarboxylic acid "versatic acid 1519") have been examined in the solid state and/or in solution. Solution spectra were simpler, being free of lattice vibrations found in the solid, but solvent bands and fluorescence phenomena were a problem. The position and relative intensity of the Raman bands are given in Table 7.5. In each of the spectra for strontium-bound DC18C6 adducts, a polarized low-energy band at ca. 260 cm⁻¹ is assigned to a Sr-O stretching or motion arising from symmetrically coordinated crown ether. A tentative assignment is also made for the crown ether ring "breathing" motion to the peaks in the region 780 to 850 cm⁻¹ that were observed for each adduct as well as for the free crown ether. Together with the infrared experiments, these data suggest that the strontium is bound within the crown ether cavity whether the complex exists as a solid or in solution.

1. Oak Ridge Associated Universities
Post-Doctoral Fellow.
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and R. Savoie, Can. J. Chem. **62**, 2293-2298
(1984).

Table 7.5. Raman bands of DC18C6 and DC18C6 adducts with various strontium salts in solution^a

DC18C6 (uncmp.)	DC18C6 SrCl ₂	DC18C6 Sr(NO ₃) ₂	DC18C6 ^b Sr(piv.) ₂	DC18C6 Sr(vers.) ₂	Assignments
	257(s)	256(s)	259(s)	c	Sr-O (ce)
786(s)	791(s)	792(w)	793(s)	792	
810(m)	806(m)	805(m)	807(m)	805	crown ether ring motions
843(m)	835(m)	834(m)	833(m)		
	913(m)	864(m)	859(w)		

s = strong; m = medium; w = weak

^aSrDC18C6(versate)₂ in CCl₄ solvent, all others in MeOH/H₂O.

^bBands due to the pivalate ion are excluded from the table.

^cThe region in which this band is expected was obscured by overlapping solvent bands.

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7.2.5 NMR and IR Studies of Alkaline-Earth Crown Ether Complexes in Solution

(R. M. Kessler,¹ J. H. Burns)

From a model system representing synergistic extraction of alkaline earths by crown ethers and alkyl phosphoric acids, two complexes have been prepared: $\text{Ba}(\text{DBP})_2 \cdot \text{H}_2\text{O} \cdot 18\text{-crown-6}$ and $\text{Sr}(\text{DBP})_2 \cdot \text{H}_2\text{O} \cdot 18\text{-crown-6}$, in which DBP=dibutylphosphate. Analyses of crystal structures have provided a complete description of their molecular geometry in the solid state (Section 7.3). In order better to understand the nature of these molecules under conditions nearer to those of solvent extraction, we have examined them in solution by infrared and NMR spectroscopy.

The NMR spectra of each of these complexes and of HDBP and 18-crown-6, separately and as a mixture, were all measured in CDCl_3 solutions. No discernible interaction was found between 18-crown-6 and HDBP, but the spectra of the complexes showed identical changes from

those of the components. The resonance due to the 24 protons of the ether is shifted from a sharp peak at 3.71 ppm downfield by about 0.2 ppm and broadened. The quartet due to the methylene protons next to the OP group in HDBP are shifted from 4.03 ppm upfield by about 0.2 ppm, overlapping the ether peak. The other DBP resonances are not shifted measurably.

The IR spectra of these complexes in CHCl_3 solution, Fig. 7.5, were compared to those of solutions of HDBP and 18-crown-6. Small but significant changes in some absorptions occurred on complexation. The C-O stretch of the ether at about 1105 cm^{-1} is shifted to lower frequencies by about 20 cm^{-1} in the complexes; this was also found in other crown-ether complexes, e.g. La (Ref. 2), Sn (Ref. 3). Also there are changes in the DBP portion of the spectrum.⁴ The P=O stretch at 1230 cm^{-1} (br) and the P-O stretch at 1040 cm^{-1} (br) are replaced by sharp peaks at 1020 cm^{-1} and 1035 cm^{-1} as the DBP ligands are complexed.

From these observations on solutions we conclude that there exist bonded complexes

Fig. 7.5. Single-beam FTIR spectra of $\text{Ba}(\text{DBP})_2 \cdot \text{H}_2\text{O} \cdot 18\text{-crown-6}$ and $\text{Sr}(\text{DBP})_2 \cdot \text{H}_2\text{O} \cdot 18\text{-crown-6}$ in CHCl_3 solution. Absorption maxima are designated E = ether, D = DBP, dibutylphosphate, and H = H_2O . Unlabelled peaks are either CHCl_3 or CO_2 in the background.

between Ba^{2+} , Sr^{2+} ions and 18-crown-6 and DBP⁻ ions in solution and suggest that the complex molecules are not very different from the ones in the crystals. The fate of the H_2O molecule in solution is not certain; although there is some indication in the IR spectra of H_2O in the 3400 cm^{-1} region.

1. Oak Ridge Associated Universities Post-Doctoral Fellow.
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3. P. A. Cusack, B. N. Patel, P. J. Smith, D. W. Allen and I. W. Nowell, J.C.S. Dalton, 1239 (1984).
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7.2.6 Extraction of Al^{3+} by Dibenzoylmethane (C. F. Baes, Jr.)

An effort has been initiated to investigate the hydrolysis of selected aqueous metal ions by solvent extraction. Many attempts have been made previously by others to use this method, but with limited success because of complications in the chemistry of the extractants used. If sufficiently simple extractant systems can be found, they would be well suited to the study of metal ion hydrolysis in solutions too dilute to be investigated by the usual methods.

A β -diketone, dibenzoylmethane (DBM) in toluene has been chosen as the extractant. The β -diketones exhibit relatively simple and predictable chemistry in the extraction of a wide variety of metal ions,¹ and the one chosen exhibits a very low distribution to aqueous solutions from a solvent such as toluene.

Al^{3+} was selected as the first metal ion to be studied because the hydrolysis of this important ion in dilute aqueous solution is not adequately known. The only significant extraction complex should involve one Al^{3+} ion and three DBM ligand anions. In acid solutions the extraction reaction should be

(wherein X^- is the anion formed by DBM). If this is the case, then the extraction coefficient (D) for Al^{3+} from sufficiently dilute aqueous solutions of controlled ionic strength will be given by

$$D = \frac{K[\text{HX}]^3/[\text{H}^+]^3}{1 + \sum K_y/[\text{H}^+]^y}$$

wherein K is the equilibrium constant for the above extraction reaction and K_y is the equilibrium constant for the general hydrolysis reaction

If the aqueous $\text{Al}(\text{III})$ concentration is sufficiently small, the formation of polynuclear hydroxide complexes in solution and the precipitation of aluminum hydroxide can be avoided.

The measurements were performed in 1 M KCl at room temperature, with 0.025 M dibenzoylmethane in toluene as the extractant. At pH values up to 4, equilibrium could not be attained after many days of shaking the two phases together. Equilibrium appears to have been approached in five measurements in the pH range 4.5 to 8 (Fig. 7.6). D showed about the pH dependence to be expected from the fairly accurately known stabilities of AlOH^{2+} and $\text{Al}(\text{OH})_4^-$ and gave a value for K close to that expected from literature data.¹ In future measurements, the dependence of D on pH will be examined closely in the range 5 to 7 in an effort to determine the stability of the poorly known intermediate hydrolysis products $\text{Al}(\text{OH})_2^+$ and $\text{Al}(\text{OH})_3(\text{aq})$.

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2. C. F. Baes, Jr. and R. E. Mesmer, The Hydrolysis of Cations, John Wiley Interscience, 1976.

Fig. 7.6. Dependence on pH of Al(III) extraction from 1 M KCl by dibenzoylmethane (HX) in toluene. The upper curve is calculated assuming AlOH^{2+} and Al(OH)_4^- to be the only aqueous hydrolysis products of Al^{3+} . The middle and lower curves show the effect of additional but uncertain species, Al(OH)_2^+ and Al(OH)_2^+ plus $\text{Al(OH)}_3(\text{aq})$, respectively.

7.2.7 Extractive Properties of Di(2-ethylhexyl)sulfoxide

(B. A. Moyer, C. E. Caley,¹ W. J. McDowell, C. F. Baes, Jr., G. N. Case)

Virtually all of the common extractants for metals also extract water, yet little is known about the hydrated forms of the extractants in solution. These hydrates are important because (1) the process of extracting a metal requires breaking bonds between the extractant and its bound water, (2) changes in hydrate composition induced by changes in water activity alter other system equilibria, and (3) hydrogen bonding involving water can provide the "glue" that stabilizes aggregated species in nonpolar solution.

In our recent efforts to characterize the extractive behavior of di(2-ethylhexyl)sulfoxide (DEHSO), we have been examining the nature of the hydrated forms of DEHSO in wet dodecane. Our primary motivation for the study was to establish whether the "nonideal" behavior of DEHSO solutions in vapor-phase osmometry experiments

could be attributed to nonspecific activity effects or, as is more usual, to aggregation phenomena. In the experiments, a series of equilibrations at 25° were performed in which 0 to 0.4 M solutions of DEHSO in dodecane were equilibrated with pure water containing optionally tritium tracer and/or nonextractable CaCl_2 . The solvent phases were then analyzed for their water content by Karl-Fischer titration or tritium scintillation counting; FTIR spectrophotometry was used to examine the vibrations of the bound water.

Equilibrium analysis of the water content of the solvent as a function of DEHSO concentration and water activity was performed using a least-squares Fortran program (Sect. 7.2.1) to fit the data to postulated hydrated species of the form $(\text{DEHSO})_m(\text{H}_2\text{O})_n$, denoted (m,n). The analysis indicated that the major hydrated species is (1,1) with an additional dimeric species tentatively identified as (2,2). For confirmation of these results, vibrational spectra of the water bound to DEHSO were collected as a function of DEHSO concentration at a water activity of unity (Fig. 7.7). An analysis of the increase in absorbance of these water bands with DEHSO concentration confirmed the major conclusion from equilibrium analysis that the predominant hydrate is a monomer with minor formation of a dimer. The analysis also permits both spectra to be resolved despite the fact that peaks due to the dimer are almost completely concealed beneath the monomer absorption.

Overall, the results are valuable in that (1) they provide an explanation for "nonideal" DEHSO behavior based on dimerization, (2) the derived formation constants may now be used to quantify other DEHSO extraction data, and (3) the observance of a hydrated DEHSO dimer provides support for the existence of similar species postulated for related neutral oxygen-donor extractants such as TPB and TOPO.

1. GLCA/ACM Science Semester student from Carleton College, Northfield, Minnesota.

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Fig. 7.7. Fourier transform infrared spectra of hydrated Di-2-ethylhexylsulfoxide (DEHSO) in dodecane as a function of DEHSO concentration at unit water activity. The peaks shown are due to the vibrations of the hydrogen-bonded ($3650 - 3150 \text{ cm}^{-1}$) and non-bonded (3687 cm^{-1}) OH groups of bound water. In order of increasing absorbance, the spectra correspond to the DEHSO concentrations 0.01, 0.02, 0.04, 0.06, 0.08, 0.1, 0.2, and 0.4 M (room temperature using a 1 mm CaF_2 cell).

7.3 Crystal Structure of

$\text{Sr}(\text{dibutylphosphate})_2 \cdot \text{H}_2\text{O} \cdot 18\text{-Crown-6}$

(J. H. Burns)

Interest in this complex arises from the fact that mixtures of crown ethers and alkyl phosphoric acids are known to synergistically extract a variety of mono- and divalent cations from aqueous solution.¹⁻³

Additionally, in the case of alkali ions at least, the more effective extractions are obtained when there is a close match between crown size and cationic radius. The geometrical relations in complexes between alkali ions and crown-ether molecules are already well characterized, but much less has been done with alkaline earths.

In order to examine in detail the bonding between alkaline-earth ions and crown ethers in synergistic-extraction combinations two model systems have been studied. These include 18-crown-6 ($\text{C}_{12}\text{H}_{24}\text{O}_6$) representing the flexible crown ethers, dibutylphosphoric acid (HDBP), and Sr^{2+} and Ba^{2+} ions (radius 1.28 and 1.47 Å, respectively). The structure of the complex formed with Ba^{2+} ions was reported earlier,⁴ and the analogous structure containing Sr^{2+} ions is presented here.

Crystals were made by reacting $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ with HDBP and 18-crown-6 and were analyzed by x-ray diffraction methods to establish both the composition and structure. The crystals are monoclinic, $\text{P}2_1/\text{c}$, with $a = 9.23(1)$, $b = 27.24(3)$, $c = 31.55(3)$ Å, and $\beta = 94.95(6)^\circ$. There are 8 molecules of $\text{Sr}(\text{DBP})_2 \cdot \text{H}_2\text{O} \cdot 18\text{-crown-6}$ in the unit cell and $d_{\text{calc.}} = 1.33 \text{ g cm}^{-3}$.

The asymmetric unit of the structure is shown in Figure 7.8. It consists of two similar but not identical molecules of the complex. In each the Sr^{2+} ion is bonded to six O atoms of the crown, to two DBP^- ions and to one H_2O molecule. For these three types of interactions the average Sr-O distances are 2.74, 2.45 and 2.63 Å, respectively. These are shorter by the difference in cationic radii than the corresponding Ba-O values in $\text{Ba}(\text{DBP})_2 \cdot \text{H}_2\text{O} \cdot 18\text{-crown-6}$, which has a quite similar molecular configuration. The closer

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Fig. 7.8. Stereoscopic drawing of two molecules of $\text{Sr}(\text{DBP})_2 \cdot \text{H}_2\text{O} \cdot 18\text{-crown-6}$ representing the asymmetric unit of the crystal structure. All atoms bonded to Sr or P are O atoms. The remaining unlabelled atoms are C.

approach of all six crown O atoms to the Sr^{2+} ion is achieved by distortion of the ring beyond what was required in the Ba^{2+} complex. In each case the cation is not in the ring but off to one side, and the ring is bent into a boat-like shape to make all its O atoms available to bond to the cation.

Calculations⁵ of the molecular energy of these two complexes show clearly that for complexation of Sr^{2+} and Ba^{2+} ions by a flexible 18-membered crown such as $\text{C}_{12}\text{H}_{24}\text{O}_6$, the electrostatic contributions far outweigh the strain energy of the crown. Thus, for such a crown there should be much less selectivity between these ions than for a rigid ligand such as dibenzo-18-crown-6.

[20]ane-(PO)₄O₂

[20]ane-(PO)₄O₂. In the synthesis two 2-chloroethyl ethers are condensed with two 1,3-bis(phenylphosphino)propanes in the presence of a base; after work up, the product is oxidized to give the tetraphosphoryl compound. The macrocycle is unreactive toward alkali metal, alkaline earth or transition metal ions in solution; however, the reaction of [20]ane-(PO)₄O₂ with lanthanide ions in acidic aqueous solution produces white flocculent precipitates that become glassy solids upon drying. The glasses are uncharacterized because the presence of all five unresolved isomers in the reaction mix appears to prevent the formation of any single crystalline species. Investigation continues into the feasibility of separating the isomers.

A crown ether with an ionizable side chain, a "lariat ether", is another attractive macrocyclic system with potential for solvent extraction. One lariat ether, sym-dibenzo-14-crown-4-oxymethyl (phenylphosphinic acid), sym-DB14C4-PO₂H, is

sym-DB14C4-PO₂H

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7.4 Synthesis of New Extractants

7.4.1 Synthetic Studies of Macrocyclic Extractants

(R. M. Kessler¹)

A desirable potential solvent extraction agent for lanthanide or actinide ions is one which combines the characteristics of phosphine oxides with the macrocyclic effect for strong binding of the ions. A synthetic scheme based on the work of Ciampolini et al.,² produces 1,7,11,17-tetraphenyl-4,14-dioxa-1,7,11,17-tetraphosphorylcycloelcosane,

being studied. A condensation is used to prepare the molecule;

sym-dibenzo-14-crown-4-hydroxide³ is treated with bromomethyl(isopropoxyphenyl)phosphine oxide and base followed by acid hydrolysis to give the crown ether with a phosphinic acid side chain. It is expected that, due to the small ring size, lithium will be complexed more strongly than the other alkali metals; investigations of the reactions of various alkali metal hydroxides with the macrocycle are in progress.

1. Oak Ridge Associated Universities Post-Doctoral Fellow.
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7.4.2 Attempt to Synthesize a Cyclic β -Diketone

(C. F. Baes, Jr.)

The β -diketones can under the proper conditions complex and extract most of the cations of the Periodic Table. Recently Tabushi et al.¹ reported the synthesis of a cyclic α -diketone

I

1,3,9,11,17,19-cyclotetracosanehexone. A model of this molecule in the enol form and triply ionized suggests that the six oxygen atoms could be directed toward a cation in the central cavity to give an approximately octahedral coordination. This compound thus offers promise as a hexadentate ligand that

can form electrically neutral and possibly extractable complexes with suitably-sized trivalent cations. Accordingly an effort has been underway to prepare gram quantities of it.

The procedure consists of first preparing 7-octynoic acid by reaction of 6-bromohexanoic acid with sodium acetylide in liquid ammonia.² This is converted to 7-octynoyl chloride and reacted with 1,8 nonadiyne to produce II and III

which are separated by chromatography on alumina. Either one or both together are reacted with pimeloyl chloride

at high dilution in CH_2Cl_2 in the presence of AlCl_3 to produce a cyclized product. This is hydrolyzed to I, which is then separated by chromatography on silica.

The entire procedure has been carried out, but no final product has yet been obtained, probably because the chromatographic separations were not sufficiently complete. HPLC and NMR analysis suggest that a clean fraction of III has since been obtained. This has been reacted with pimeloyl chloride and worked up to produce a material that is ready for the final chromatographic separation.

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8. CATALYSIS

The redox characteristics of selected arenes and heterocyclic aromatics in liquid $\text{EMI}(\text{Al}_2\text{Cl}_7)$ (EMI = 1-ethyl-3-methyl-1H-imidazolium cation) at 25°C were investigated by means of cyclic voltammetry and optical spectroscopy. Anthracene (An), perylene (Pe), and 9,10-diphenylanthracene (DPA) dissolved without complex formation, and underwent a minor (3% in 24 h) proton mediated catalytic decomposition. 9H-Phenothiazine (PTZ) and 9H-phenoxazine (POZ) dissolved with reversible solvo complex formation and without perceptible decomposition (24 h). Spontaneous oxidation of these arenes and heteroaromatics to radical cations previously reported by others was not observed in our melts. When oxidized electrochemically, DPA, POZ and PTZ underwent reversible one-electron oxidations to their respective radical cations, $\text{DPA}^{+\bullet}$ (very persistent), $\text{POZ}^{+\bullet}$ (stable) and $\text{PTZ}^{+\bullet}$ (stable). Oxidation of $\text{DPA}^{+\bullet}$ was irreversible while the one-electron oxidations of $\text{POZ}^{+\bullet}$ and $\text{PTZ}^{+\bullet}$ to POZ^{2+} and PTZ^{2+} were reversible and the dications were stable (24 h). The one-electron oxidation of An was quasi-reversible while oxidation of Pe yielded a solid product. For purposes of this investigation a synthesis was developed for EMICl which upon reaction with AlCl_3 yielded liquid $\text{EMI}(\text{Al}_2\text{Cl}_7)$ of exceptional purity (0.1-0.2 mM protic impurities, no perceptible oxidizing impurities). The catalytic decomposition chemistry of naphthalene (Na), pyrene (Py), An, naphthalene (Nc), 9,10-dihydroanthracene (DHA), and diphenylmethane (DPM) in molten AlCl_3 -NaCl-KCl (60-26-14 m/o) at 120°C was investigated by means of ESR, $^1\text{H-NMR}$ and quench and separation procedures. Solutions of Na and Py were stable; An, Nc and DHA underwent a slow hydrogen transfer/disproportionation, while DPM underwent a fast transalkylation. Radical cation formation was not detected by ESR. As an aid to others in the development of an analytical procedure for oxide determination in chloroaluminate melts we investigated the reduction of Ta(V) in AlCl_3 - EMICl (44-56 m/o) by cyclic voltammetry and by optical spectroscopy of solutions reduced by bulk coulometry.

A program to study structure and catalytic properties of solid surfaces is described in Section 8.2. This program at present incorporates two approaches. One approach, still in technical development, has the ultimate goal of correlating catalytic reactivity and selectivity under realistic conditions with the structure and composition of the model catalytic surfaces as determined by using various surface analytical techniques. An apparatus, now nearly complete, has been developed for this purpose and is described in Section 8.2.1. A second part of this program, which has been in progress for several years, focuses on the application of low energy alkali ion scattering as a probe of surface structure. The use of this technique to study surface layer relaxation on clean Mo(111) and to characterize adsorption of S on Mo(111) are described in Sections 8.2.2 and 8.2.3. Previous ion scattering studies of amorphous metal surfaces have led to further x-ray photoemission and Auger electron spectroscopic characteristics of these surfaces as discussed in Section 8.2.4. Finally, initial experiments to use multi-charged ions as novel probes of surface properties are discussed in Section 8.2.5.

8.1 Reactions and Catalysis in Molten Salts

8.1.1 Synthesis of Ultrapure

1-Ethyl-3-methyl-1H-imidazolium Chloride¹ and the Preparation and Characterization of Its Molten Mixtures With Aluminum Chloride

(S. P. Zingg, R. M. Pagni, G. P. Smith)

Fused salts that are liquid at room temperature or below comprise an unconventional but interesting class of aprotic solvents for studying the chemistry of inorganic, organome-

tallic and organic solutes.²⁻⁶ Of particular interest has been the development of melts composed of AlCl_3 and

1-ethyl-3-methyl-1H-imidazolium chloride (EMICl) which are liquid at 20°C or less over the range of AlCl_3 mole fractions extending from 0.35 to 0.66.⁵ Attractive features of this molten salt system, in addition to its low melting temperature, are a wide range of Lewis acidity, an especially wide electrochemical window and a UV cutoff below 240 nm.

AlCl_3 -EMICl mixtures are nonprotic, ionized solvents.

The AlCl_3 -EMICl molten salt systems appear ideally suited for studying the oxidations of organic species by spectroscopic and electrochemical techniques. Previous work with this system has, however, been plagued by the presence of impurities, especially protic and oxidizing impurities. In order to utilize AlCl_3 -EMICl mixtures as solvents in our investigations of radical cations and dications, we required large quantities of the organic salt in a much purer form.

The previous synthesis of the very hygroscopic EMICl was performed by first condensing ethyl chloride (b.p. 12.27^{760}) into a glass pressure vessel containing 1-methylimidazole, then heating the mixture at 75°C for two days, and finally recrystallizing the resulting solid from acetonitrile/ethyl acetate. Besides the inherent danger in running a reaction at high pressures, this procedure cannot easily be performed on a large scale. Furthermore, the use of ethyl acetate as a recrystallization solvent was undesirable since it has been found that ethyl acetate cannot be removed completely from a similar organic salt (N-(1-butyl)pyridinium chloride, BPCl) even after extensive heating under vacuum.⁷

A new procedure has been developed for the preparation of EMICl which circumvents the problems inherent in the previous procedure and produces high purity EMICl in large quantities. Gaseous ethyl chloride was slowly bubbled through a solution of 1-methylimidazole in acetonitrile at 70°C under an argon atmosphere. Crystallization from dry acetonitrile followed by recrystallization from the same solvent under argon yielded the pure, anhydrous organic chloride which proved ideally suited for the preparation of the molten salts containing aluminum chloride. We have synthesized 600 g batches of EMICl by this procedure and see no reason why the compound cannot be prepared on a kilogram or larger scale.

EMICl prepared by this method had a melting point of $87.0\text{--}87.8^\circ\text{C}$ (corr.) (lit.⁵ $82\text{--}87^\circ\text{C}$). The ^1H NMR spectrum showed no trace of impurities.

Using EMICl from the improved procedure and ultrapure AlCl_3 prepared as previously described,⁷ AlCl_3 -EMICl melts were prepared with the following compositions: 44-56 m/o and 67-33 m/o. These systems were characterized by UV-visible spectroscopy and cyclic voltammetry. Neither melt composition displayed any absorption in either the UV or visible region above the short wavelength cutoff of 236 nm and 233 nm ($\lambda = 57\mu\text{m}$) for the 44-56 and 67-33 m/o AlCl_3 -EMICl melts, respectively. The absorption cutoffs were sharp. These melts had previously been reported to be useful only to ca. 320 nm.⁵

Background cyclic voltammograms for the AlCl_3 -EMICl melts were measured at both glassy carbon ($d = 3\text{ mm}$) and tungsten ($d = 4\text{ mm}$) disk electrodes. Potentials were referenced to an Al wire electrode submerged in a 67-33 m/o AlCl_3 -EMICl melt saturated with AlCl_3 and separated from the bulk solution by a quartz frit. The observed electrochemical windows (-2.0 to $+0.8\text{ V}$ on glassy carbon and -2.1 to $+0.7\text{ V}$ on tungsten for the 44-56 m/o melt, and -0.1 to $+1.7\text{ V}$ on glassy carbon and $+0.3$ to $+2.4\text{ V}$ on tungsten for the 67-33 m/o melt) were similar to those observed by Wilkes et al.⁵ and Karpinski et al.⁸ Cyclic voltammograms previously reported^{5,8} for AlCl_3 -EMICl mixtures showed the presence of large amounts of impurities, presumably H_2O or other protic impurities and/or oxidant impurities. Backgrounds CV's on melts prepared in this laboratory showed no evidence of impurities at detection limits much lower than those employed in the previous work.

The stability of molecular anthracene in acidic $\text{AlCl}_3\text{-BPCl}$ (67-33 m/o) melts has been shown to be particularly sensitive to the presence of protic and oxidizing impurities.⁷ The UV-visible spectrum of anthracene in the $\text{AlCl}_3\text{-EMICl}$ 67-33 m/o melt at 25°C was measured after approximately 1 h of mixing in an inert atmosphere glovebox. Dissolution of the anthracene was slow. This experiment was repeated four times with anthracene concentrations ranging from 19 to 21 mM. The only spectral bands observed were those of anthracene and a small amount of protonated anthracene. The concentration of anthracenium ion present (0.3 to 0.7 mM) was estimated using the ϵ value ($34,500 \text{ M}^{-1} \text{ cm}^{-1}$) of the band maximum measured for the anthracenium ion in $\text{SbCl}_3\text{-AlCl}_3\text{-BPCl}$ (60-22-18) at 25°C.⁷ No evidence of oxidation of anthracene was observed. Over a period of 24 h the amount of protonated anthracene increased only slightly (by 0.1-0.2 mM) with an equivalent decrease in the anthracene concentration. Similar studies with perylene and other substrates that form stable radical cations in the presence of oxidants in $\text{AlCl}_3\text{-EMICl}$ (67-33 m/o) showed no radical cation formation without deliberately added oxidants. (See the following two Sections.) These experiments demonstrated that the amount of protic impurities from all sources was very low and that oxidizing impurities were not present at any measurable level.

The above procedure greatly facilitated the preparation of ultrapure 1-ethyl-3-methyl-1H-imidazolium chloride in large quantities. Spectroscopic and electrochemical studies of $\text{AlCl}_3\text{-EMICl}$ melts prepared from this material demonstrated the effectiveness of this procedure in producing high quality EMICl.

1. The compound is commonly, but incorrectly, called 1-methyl-3-ethylimidazolium chloride.
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4. M. Lipsztajn and R. A. Osteryoung, J. Electrochem. Soc. 130, 1969 (1983).
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6. J. Robinson and R. A. Osteryoung, J. Am. Chem. Soc. 101, 323 (1979).
7. S. P. Zingg, A. S. Dworkin, M. Sørli, D. M. Chapman, A. C. Buchanan III, and G. P. Smith, J. Electrochem. Soc. 131, 1602 (1984).
8. Z. J. Karpinski and R. A. Osteryoung, Inorg. Chem. 23, 1491 (1984).

8.1.2 Electrochemistry and Optical Spectroscopy of Some Arenes and Heteroaromatics in Chloroaluminate Melts at Ambient Temperatures

(S. P. Zingg, A. S. Dworkin, R. M. Pagni, G. P. Smith)

A preliminary investigation was made of the redox characteristics of anthracene (An), perylene (Pe), 9,10-diphenylanthracene (DPA), 9H-phenothiazine (PTZ), and 9H-phenoxazine (POZ) at ambient temperatures in liquid mixtures of AlCl_3 and 1-ethyl-3-methyl-1H-imidazolium chloride (EMICl) with the composition 67-33 m/o. Some of the same measurements were also carried out in liquid mixtures of AlCl_3 and N-(1-butyl)pyridinium chloride (BPCl) with the composition 67-33 m/o. Very similar results were obtained with both media. For purposes of brevity, numerical data cited here are limited to $\text{AlCl}_3\text{-EMICl}$ melts.

AlCl_3 mixed with EMICl or BPCl in the proportions 67-33 m/o undergoes a highly exothermic reaction to form an ionic liquid with the nominal compositions $\text{EMI}(\text{Al}_2\text{Cl}_7)$ or $\text{BP}(\text{Al}_2\text{Cl}_7)$, respectively. These liquids glassify at temperatures well below ambient. Both liquids have high AlCl_3 activities. Liquid $\text{EMI}(\text{Al}_2\text{Cl}_7)$, in particular, has an AlCl_3 activity at room temperature that is

very close to unity, the highest value possible.

It has been reported¹ that oxidizable arenes, such as those we investigated, are spontaneously oxidized to form persistent radical cations in BP(Al_2Cl_7), EMI(Al_2Cl_7) and various other media with high AlCl_3 activity. This is almost certainly an impurity effect. In our carefully purified melts spontaneous oxidation of the arenes and the more oxidizable heteroaromatics to radical cations was not observed when UV-VIS spectroscopy was employed under conditions in which oxidation of a few per cent of the solute would easily have been detected. When the substrates in these melts were deliberately oxidized, strong and quite persistent radical cation spectra were observed except for An.

An, Pe, and DPA dissolved in EMI (Al_2Cl_7) as neutral molecules without any sign of sigma complex formation (for spectral details see Table 8.1). However, we did find spectroscopic evidence of a small amount of arenium ion formation for An and DPA indicative of 0.3-0.7 mM protic impurities. After standing 24 h, the UV-VIS spectra of An, Pe and DPA in EMI(Al_2Cl_7) each showed a very small degree of decomposition with a loss of about 3% of the initial concentration. We attribute this decomposition to reactions catalyzed by trace protic impurity. The more complex spectral and electrochemical behavior of the heteroaromatics

PTZ and POZ is discussed in Section 8.1.3.

Each of the three arenes was investigated by cyclic voltammetry (CV) at a glassy carbon electrode ($d = 3 \text{ mm}$) with potentials referenced to $\text{Al}/\text{EMI}(\text{Al}_2\text{Cl}_7)$, sat'd AlCl_3 . A 1.74 mM solution of DPA at $25 \pm 1^\circ\text{C}$ was oxidized in a Nernstian one-electron process at scanning rates of 5-500 mV s^{-1} with $E_{1/2} = 0.992 \text{ V}$ as measured by ΔE_p , $E_p^C - E_p/2^C$ and $E_p^A - E_p/2^A$. At the fastest scan rates an approximately 10% drop in the peak current ratio, i_p^C/i_p^A , indicated a reversible equilibrium involving the DPA radical cation ($\text{DPA}^{+\bullet}$). One possibility is an equilibrium between two radical cation isomers, one of which is formed by an intramolecular condensation between the 9-phenyl group and the 1 position on the anthracene group. Further oxidation of $\text{DPA}^{+\bullet}$ followed an irreversible course.

The long-term persistence of $\text{DPA}^{+\bullet}$ was examined by UV-VIS observations (see Table 8.1) on a solution of DPA which had been partially oxidized (~50%) by bulk coulometry. In 24 h the concentration of $\text{DPA}^{+\bullet}$ decreased by only 12% and was accompanied by the formation of a significant quantity of 9,10-diphenyl-1H-anthracenium cation (DPAH^+). It is assumed that the latter was produced by a condensation/protonation reaction.

The electrochemical oxidation of Pe yielded an insoluble product. In a partial bulk coulometry experiment the oxidized product occurred as a black precipitate and UV-VIS spectroscopy of the solution phase, following filtration, showed only unoxidized Pe.

CV of An showed a quasireversible oxidation to $\text{An}^{+\bullet}$ at about 1.1 V followed by a second, irreversible oxidation at about 1.8 V. UV-VIS spectra following partial, bulk coulometry showed the formation of the 1H-anthracenium cation, presumably due to a condensation/protonation reaction.

Table 8.1. UV-Visible absorption bands for An, Pe, DPA and $\text{DPA}^{+\bullet}$ in EMI(Al_2Cl_7)

	λ, nm ($10^{-3}\epsilon$, $\text{M}^{-1} \text{ cm}^{-1}$)
An	340 (4.74), 360 (7.05), 380 (6.35)
Pe	254 (35.3), 372 (4.10), 390 (10.8), 412 (23.3), 440 (30.1)
DPA	357 (5.72), 377 (9.42), 397 (9.54)
$\text{DPA}^{+\bullet}$	258 (90.1), 322 (47.9), 340 (18.9) 362 (21.0), 585 (13.1), 655 (13.0) 725 (11.6)

1. E.g.; (a) J. Robinson and R. A. Osteryoung, J. Amer. Chem. Soc. **101**, 323 (1979), (b) C. P. Keszthelyi, Electrochem.

Acta. **26**, 1261 (1981), (c) H. Bock and W. Kaim, Acc. Chem. Res. **15**, 9 (1982), (d) A. J. Bard, A. Ledwith and H. J. Shine, Adv. in Phys. Org. Chem. **13**, 155 (1976), (e) J. J. Rooney and R. C. Pink, Chem. Soc. Proc., 142 (1961).

8.1.3 Evidence for Aluminum Chloride Complexation of Phenothiazine and Phenoxazine in AlCl_3 -1-Ethyl-3-methyl-1H-imidazolium Chloride Melts

(S. P. Zingg, A. S. Dworkin, R. M. Pagni, G. P. Smith)

Spectroscopic and electrochemical studies of 9H-phenothiazine (PTZ) and 9H-phenoxazine (POZ) in AlCl_3 -1-ethyl-3-methyl-1H-imidazolium chloride (EMICl) melts indicate that these heterocyclic aromatics react with Al_2Cl_7^- to form N-Al and chalcogen-Al bonds in melts containing excess AlCl_3 . AlCl_3 functions as a Lewis acid forming complexes with a great variety of Lewis bases including amines,¹ ethers² and thioethers.³ This is one of the most important aspects of the chemistry of AlCl_3 and plays an extensive role in its use as a catalyst in Friedel-Crafts and related reactions.

Metal-ion interactions with phenothiazine and its derivatives have been extensively studied.⁴ However, few genuine coordination complexes (none containing Al) have been isolated and the coordination chemistry of PTZ has not been thoroughly explored. A few transition metal complexes of PTZ have been prepared in which the heterocycle is bonded to the metal through the sulfur atom.⁵ These complexes are of particular interest because of the electron transport properties of partially oxidized complexes. Complexation of PTZ as well as POZ by SbCl_3 has been proposed to explain the slow rates of oxidation of the heterocycles to radical cations and diradicals in SbCl_3 -rich molten salt systems.⁶ SbCl_3 appears to complex PTZ and POZ at both nitrogen and the chalcogen atom. Coordination complexes of POZ have not been reported.

The UV-visible spectra of POZ and PTZ were measured in basic (44-56 m/o) and acidic

(67-33 m/o) AlCl_3 -EMICl melts (see Fig. 8.1). In the basic melt the spectra were quite similar to the corresponding spectra in organic solvents (see Table 8.2). However, the spectra for both PTZ and POZ in the acidic melt were drastically different from those obtained in the basic melt and in organic solvents. No additional bands were observed in the visible region for either POZ or PTZ in AlCl_3 -EMICl melts. The initial spectra did not change over a 24 h period.

The spectra observed in the basic melt for POZ and PTZ were consistent with the effect of amino group substitution on a benzene ring. The amino group produces a large effect due to conjugation of the nitrogen lone pair with the ring system: i.e., bathochromic shift, increased intensity, and decreased fine structure. The loss in fine structure is usually quite drastic and a large broad band appears at longer wavelength. However, protonation or quaternization of the amino group destroys the conjugation effect resulting in only a slight bathochromic shift and a slight decrease in

Fig. 8.1. UV-visible absorption spectra for phenothiazine (8 mM) and phenoxazine (8 mM) in both 67-33 and 44-56 m/o AlCl_3 -EMICl at $25 \pm 1^\circ\text{C}$ together with the spectra of the solvents. All spectra referenced against air ($\lambda = 60 \mu\text{m}$).

Table 8.2. UV-Visible absorption bands for POZ and PTZ

Substrate	Medium	λ , nm ($10^{-3} \epsilon$, M ⁻¹ cm ⁻¹)
PTZ	AlCl ₃ -EMICl (44-56 m/o)	257 (39.0), 318 (4.43)
	CH ₃ CN ^a	254 (53.7), 320 (5.13)
	CH ₃ CN ^b	254 (45.7), 318 (4.79)
	CH ₃ CN ^c	254 (50.1), 317 (3.98)
	AlCl ₃ -EMICl (67-33 m/o)	248 (4.50), 270 (1.37), ~290 (sh)
POZ	AlCl ₃ -EMICl (44-56 m/o)	<245, 317 (8.07)
	CH ₃ CN ^b	239 (45.7), 317 (8.51)
	CH ₃ CN ^c	238 (39.8), 315 (7.94)
	AlCl ₃ -EMICl (67-33 m/o)	<245, 275 (2.31)

^aP. Hanson and R.O.C. Norman, J. Chem. Soc. Perkin II, 264 (1973).

^bM. P. Olmstead, P. N. Craig, J. F. Lafferty, A. M. Pavloff and C. L. Zirkel, J. Org. Chem. 26, 1901 (1961).

^cT. J. Kemp, P. Moore and G. R. Quick, J. Chem. Soc. Perkin II, 291 (1980).

fine structure of the spectra relative to that of the parent. The effect of an -OR or -SR group is usually not as pronounced as the effect of an amino group. The observed spectra for PTZ and POZ in AlCl₃-EMICl melts thus indicate the presence of the heterocycles as molecular species in basic melts while complexation of the nitrogen, and possibly the chalcogen atom, appears likely in acidic melts. The heterocycles are presumably complexed either by Al₂Cl₇⁻ or AlCl₃ in melts containing excess AlCl₃.

Dissolution of PTZ and POZ in acidic melts gave colored solutions, orange and pink, respectively, while solutions of both heterocycles in basic melts were colorless. When solutions of the heterocycles in acidic melts were made basic by the further addition of EMICl, the solution color disappeared. The UV-visible spectra of these solutions were identical to the spectra obtained by directly

adding PTZ or POZ to a 44-56 m/o melt. These results indicate the reversibility of the complexation reaction for PTZ and POZ in acidic AlCl₃-EMICl melts.

The results of cyclic voltammetric studies of PTZ and POZ in 67-33 m/o melts are given in Tables 8.3 and 8.4, respectively, where $\Delta E_p = E_p^a - E_p^c$ is the difference between the anodic and cathodic peak potentials, $|E_p - E_{p/2}|$ is the magnitude of the difference between the peak and half-peak potentials, $E_{1/2} = E_{p/2} + 1.09 RT/nF$, and v is the scan rate. For one electron nernstian processes the theoretical values of $|E_p - E_{p/2}|$ and ΔE_p are 56 mV and 59 mV, respectively.

The observed increase in ΔE_p at higher scan rates may be attributable to incompletely compensated resistance. However, increases in ΔE_p of this type may also indicate accompanying chemical equilibria such as complexation.⁷ Deviations of the peak current ratios

Table 8.3. Cyclic voltammetric parameters for PTZ in $\text{AlCl}_3\text{-EMICl}$ (67-33 m/o) at $25 \pm 1^\circ\text{C}^a$

ν mV s ⁻¹	ΔE_p mV	i_p^c/i_p^a	$E_p^c - E_{p/2}^c$ mV	$E_p^a - E_{p/2}^a$ mV	$E_{1/2}$ mV
PTZ $\rightleftharpoons$ PTZ ^{•+} + e ⁻					
500	81	1.04	60	64	822
200	75	1.05	60	62	821
100	70	1.04	57	61	820
50	66	1.04	57	59	823
20	63	1.02	57	59	822
10	62	1.03	57	60	822
5	59	1.01	56	57	823
bPTZ ^{•+} $\rightleftharpoons$ PTZ ²⁺ + e ⁻					
500	82	1.01	63	60	1420
200	78	1.02	62	60	1418
100	73	1.03	59	59	1418
50	69	1.02	60	57	1419
20	65	1.03	58	57	1418
10	64	1.04	58	57	1418
5	59	1.05	59	56	1418

^aConc. = 8.00 mM. Potentials measured at a glassy carbon electrode (d = 3 mm) relative to $\text{Al}/\text{AlCl}_3\text{-EMICl}$ (67-33 w/o), sat'd AlCl_3

bPTZ^{•+} produced by bulk coulometric oxidation of PTZ (0.634 equiv. passed).

(i_p^c/i_p^a) from unity do not appear to be due to reactions of the radical cations or dications since the ratios do not change as a function of the scan rate. Peak currents are also dependent upon diffusion coefficients which will be largely affected by the degree of complexation of the heterocycle and its radical cation and dication in solution. In the radical cations of PTZ and POZ, the unpaired spin density resides primarily on the nitrogen. The nitrogen lone pair is, therefore, no longer available for complexation with AlCl_3 when oxidized to the radical cation. The diffusion coefficient, D , for PTZ^{•+} or POZ^{•+} may, therefore, be smaller than D for the respective parent heterocycle. Slight increases or decreases in peak current ratios may also be indicative of electrochemical

processes accompanied, respectively, by pre- or post-equilibria: i.e., $X \rightleftharpoons R$, $R \rightleftharpoons O + e$ where R is the reduced species, O is the oxidized species and X is a compound or complex of R . The deviation in peak current ratios from unity is especially large for the POZ^{•+}/POZ²⁺ couple. This deviation may also be due to the absorption of one of the species on the tungsten electrode utilized. Significant adsorption of the parent POZ was observed on tungsten.

The CV studies indicate the reversible formation of radical cations and dications by successive one electron oxidations of PTZ and POZ. UV-visible spectra taken after bulk coulometric oxidation of solutions of PTZ and POZ in acidic melts first to the respective radical cations and then to the respective

Table 8.4. Cyclic voltammetric parameters for POZ in $\text{AlCl}_3\text{-EMICl}$ (67-33 m/o) at $25 \pm 1^\circ\text{C}^a$

v mV s ⁻¹	ΔE_p mV	i_p^c/i_p^a	$E_p^c - E_p^a$ mV	$E_p^a - E_{p/2}^a$ mV	$E_{1/2}$ mV
POZ $\rightleftharpoons$ POZ ^{•+} + e ⁻					
500	71	1.00	58	62	921
200	63	1.00	57	58	919
100	61	1.00	55	58	919
50	59	1.00	56	57	919
20	58	1.02	57	58	918
10	56	1.00	56	57	919
5	56	1.01	55	58	919
bPOZ ^{•+} $\rightleftharpoons$ POZ ²⁺ + e ⁻					
500	74	0.91	60	61	1615
200	67	0.91	57	58	1613
100	64	0.91	60	59	1614
50	62	0.93	55	59	1613
20	61	0.93	56	58	1614
10	61	0.92	56	58	1614
5	60	0.93	55	58	1614

^aConc. $\equiv$ 8.09 mM. Potentials measured at a glassy carbon electrode ($d = 3$ mm) for PTZ $\rightleftharpoons$ PTZ^{•+} and at a tungsten electrode ($d = 4$ mm) for PTZ^{•+} $\rightleftharpoons$ PTZ²⁺. All potentials relative to $\text{Al}/\text{AlCl}_3\text{-EMICl}$ (67-33 m/o), sat'd AlCl_3 .

bPOZ^{•+} produced by bulk coulometric oxidation of POZ (0.789 equiv. passed).

dications, demonstrated the stability of the radical cations and dications in these media. None of the spectra changed significantly over a period of 24 h. The wavelength maxima and molar extinction coefficients for the UV-visible bands of the radical cations and dications are given in Table 8.5.

The cyclic voltammetric behavior for PTZ was also examined in the basic melt. The PTZ/PTZ^{•+} couple is only quasireversible in this media due to follow up reactions which have not been fully explored. An $E_{1/2}$ of +0.36 V was obtained for the PTZ/PTZ^{•+} couple in the basic melt. The $E_{1/2}$ for the same couple in the acidic melt was +0.82 V. Small junction potential changes in going from basic to acidic melts can cause changes in $E_{1/2}$ but these have been shown to be

Table 8.5. UV-Visible absorption bands for the radical cations and dications of PTZ and POZ in $\text{AlCl}_3\text{-EMICl}$ (67-33 m/o) at 25°C

	λ, nm ($10^{-4}\epsilon, \text{M}^{-1} \text{cm}^{-1}$)
PTZ ^{•+}	272 (5.82), 517 (1.16)
PTZ ²⁺	290 (>5.50), 470 (1.78)
POZ ^{•+}	257 (2.52), 541 (1.96)
POZ ²⁺	266 (3.12), 480 (2.90)

very much smaller in systems of this sort.⁶ The large increase (460 mV) in the $E_{1/2}$ for the oxidation of PTZ to its radical cation in acidic melts is consistent with the formation of PTZ: AlCl_3 complexes in these media.

Complexation of the nitrogen lone-pair would make oxidation of PTZ more difficult.

Spectroscopic and electrochemical studies of PTZ and POZ in AlCl_3 -EMICl molten salt systems are consistent with complexation (presumably by chloroaluminate species) of the heterocycles in melts which contain excess AlCl_3 while in melts containing excess EMICl, PTZ and POZ are present as molecular species. Complexation of PTZ and POZ to metal ions is of interest both because of the wide use of phenothiazine and related compounds as pharmaceuticals and because of the stability of radical cations and dications of these types of heterocycles. AlCl_3 is widely utilized as a catalyst in organic synthesis where complexation to heteroatoms is often proposed. However, complexes of the type R_2XAlCl_3 (where $\text{X} = \text{O}, \text{N}$ or S) have not been well characterized. Further investigations of these novel heterocycle-chloroaluminate complexes are underway.

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8.1.4 Reactions of Some Arenes in Molten Mixtures of Aluminum Chloride, Sodium Chloride and Potassium Chloride at Elevated Temperatures

(A. S. Dworkin, G. P. Smith)

We have surveyed the reactions of a number of arenes in the strong Lewis acid melt AlCl_3 -NaCl-KCl (60-26-14 m/o) at 120°C . The component chloride salts were purified by state of the art methods and were handled on vac lines and in glove boxes with Ar atmospheres. The arenes studied were naphthalene (Na), pyrene (Py), anthracene (An), naphthacene (Nc), 9,10-dihydroanthracene (DHA), and diphenylmethane (DPM). The experimental methods applied were ESR, NMR, and quench and separation techniques.

Spontaneous oxidation reactions reported by others to take place in most chloroaluminate melts did not occur as evidenced by the absence of radical cations. Solutions of Na and Py were stable; An, Nc and DHA underwent slow hydrogen transfer/disproportionation reactions; while DPM underwent a fast transalkylation. In the reactions of An and Nc the products were hydroarenes and condensed arenes, whereas DHA gave 1,2,3,4-tetrahydroanthracene and anthracene. DPM was the only one of these arenes for which transalkylation is possible. This transalkylation reaction in melts has been reported to proceed through a predominantly Lewis acid catalyzed mechanism.¹

1. A. C. Buchanan, III, A. S. Dworkin, and G. P. Smith, *J. Am. Chem. Soc.* **105**, 2843 (1983).

8.1.5 Reduction of Ta(V) in a Basic Chloroaluminate Melt

(J. E. Coffield,¹ S. P. Zingg, G. P. Smith)

A spectroscopic and electrochemical study of the reduction of Ta(V) in liquid mixtures of AlCl_3 and 1-ethyl-3-methyl-1H-imidazolium chloride (EMICl) in the proportions (44-56 m/o) at ambient temperatures was carried out in support of an attempt by G. Mamantov and T. M. Laher (University of Tennessee) to develop an analytical method for oxide determination in chloroaluminate melts at ambient temperatures based on the use of Ta(V) as an oxide probe. Oxide is an ubiquitous impurity in AlCl_3 systems and, as such, is potentially an uncontrolled factor in proton exchange reactions in these media. Analytical procedures for oxide determination will be very useful for establishing the efficacy of methods used to remove this impurity from chloroaluminate ambient temperature melts.

Numerous methods have been put forward as analytical determinants for oxide in chloroaluminate melts but most have been shown not to work.² Those that work at all have been shown to work for some systems but not others. Laher et al.² successfully used TaCl_5 as an analytical probe for oxide in AlCl_3 -NaCl melts at elevated temperatures and, more recently, investigated the possible application of this method to ambient temperature systems. The method involves the electrochemical reduction of Ta(V) in basic melts, and these investigators found this process to differ in important respects in AlCl_3 -EMICl melts at ambient temperatures as compared with AlCl_3 -NaCl melts at elevated temperatures.

Among the differences was the observation of a transient blue color, changing to opaque brown, during the bulk coulometric reduction of green Ta(IV) solutions, which had been formed by the electrochemical reduction of Ta(V). These investigators lacked the spectroelectrochemical equipment required for a further investigation of these color changes and asked us to carry out such measurements for them. In repeated attempts we failed to

observe the transient blue color although our electrochemical data reproduced theirs quite well, differing only with respect to some very weak voltammetric peaks that might be associated with impurities.

1. Department of Chemistry, University of Tennessee.
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8.2 Surface Science and Heterogeneous Catalysis

8.2.1 Construction of an Apparatus for Surface Studies of Hydrodesulfurization Catalysis (D. R. Huntley)

A new apparatus has been custom designed and built for surface studies of hydrodesulfurization catalysis by transition metal sulfides. The apparatus is comprised of an ultrahigh vacuum (UHV) chamber coupled to a "high" pressure reaction chamber (≤ 1 atm). A schematic diagram of the system is shown in Figure 8.2.

At the heart of this system is a linear motion "wobble-stick" which facilitates the transfer of a sample between the high pressure and the UHV chambers. In the high pressure chamber, the sample can be heated by standard methods. The high pressure chamber can be pumped rapidly (100 torr to 10^{-6} torr in 1 minute) following the catalytic reactions or other high pressure treatments. The sample can then be transferred fairly quickly (1 minute) into the UHV system for surface analysis. In the UHV chamber, the sample can be heated to 1500°C by electron bombardment, cleaned by ion sputtering and dosed with various gases including S_2 . A future improvement will be to construct a liquid nitrogen cold finger for cooling the sample.

Various analytical surface spectroscopies were chosen to provide information about the bonding of adsorbates to model catalyst surfaces. The techniques currently available are Auger electron spectroscopy (AES) which provides information about the elemental

Fig. 8.2. Schematic diagram of the catalytic reaction/UHV surface analysis system. The UHV chamber is on two levels; the HREELS spectrometer is on the lower tier; the transfer assembly, mass spectrometer and CMA are on the upper tier.

composition of a surface, high resolution electron energy loss spectroscopy (HREELS) which provides vibrational spectra which are used to determine bonding symmetries and frequencies and to identify molecular fragments on the surface, and thermal desorption spectroscopy which is used to determine desorption energies and in some cases to identify molecular species present on the surface. The Auger and HREEL spectrometers have been systematically tested. A gas chromatograph (GC) has been installed and tested on-line in the high pressure chamber for monitoring reactant and product gas mixtures. All of the spectrometers and the GC will soon be interfaced to a microcomputer (IBM PC-AT) using commercial interface boards and software (Keithley).

Although full advantage of the transfer system has not yet been realized, experiments are in progress in both the UHV chamber and the high pressure chamber. Preliminary characterization of two model catalysts has begun.

Previous studies have indicated that sulfided molybdenum metal has catalytic activity for the hydrodesulfurization of thiophene.¹ Ion scattering and low energy diffraction have provided

some information on the bonding site but no HREELS study has been done. Single crystal Mo(001) has been mounted in the UHV chamber in order to further characterize the bonding of sulfur to this surface. Adsorption of sulfur containing molecules will be possible over a wide pressure range (10^{-10} to 10 torr). In addition, studies of coadsorbed S and O, and S and methyl mercaptan will be studied by HREELS.

The industrial HDS catalysts are generally complex supported molybdenum oxides which have been treated in hydrogen and hydrogen sulfide. The structure of the resulting molybdenum sulfide is thought to be similar to that of layered molybdenum disulfide. Furthermore, there is strong evidence that the catalytically active sites lie at the edges of these layers. Due to the natural anisotropy of the crystals, however, the edge plane area is small compared to the basal plane area. One way to expose additional edge area is by mild chemical oxidation or etching. Such treatments produce a surface with enhanced reactivity (essential for activity measurements on small surface area samples) and which is amenable to surface analysis.

The mild oxidation of MoS_2 and MoSe_2 is being studied in the pressure range of 10-200 torr in the high pressure chamber. The samples are heated resistively to 400-600°C for 1-100 minutes. The samples are removed and examined microscopically for evidence of oxidation. Oxidation begins at edge sites and defects, and can be observed as etch pits or extensive spiral terracing. Mild oxidation of the surfaces occurs at 450-500°C when heated in 100-200 torr of oxygen for 5 minutes. Increasing the temperature to 500-600°C results in the complete oxidation of the sample to MoO_3 . Careful control of the oxidation conditions will allow a systematic study of the effects of edge sites on the catalytic activity. These samples will ultimately be transferred to the UHV chamber for characterization by HREELS and AES.

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8.2.2 Surface Relaxation in Clean $\text{Mo}(111)$ Measured by Low Energy Alkali Ion Scattering (S. H. Overbury)

Considerable previous work has been done in this lab in measuring and analyzing alkali ion scattering from $\text{Mo}(001)$, both clean and with atomic overlayers of O, S, C and N.^{1,2} The goal is to develop ion scattering as a probe of surface structure and adsorbate bonding geometry. The scattering from adsorbate covered surfaces is largely dominated by the structure of the underlying surface. To understand this better, we have examined a clean $\text{Mo}(111)$ surface, a substrate of different surface structure and symmetry than $\text{Mo}(001)$. Previous measurements of scattering potential³ and other ion scattering effects should be applicable, and all observed differences should be related to structural differences between the two surfaces.

The ion scattering results were found to be fully consistent with a bulk terminated structure predicted by low energy electron diffraction (LEED) studies. The ion scattering

exhibited six-fold symmetry at grazing incidence consistent with the symmetry of the first atomic layer. At larger incident angle, the true three-fold symmetry is apparent, since at larger angles deeper layers contribute. These layers reduce the symmetry of the first layer.

The scattering was characterized as a function of incident polar and azimuthal angle and for various total scattering angles using 1000 eV Li^+ probe ions (Fig. 8.3). All azimuths show a critical cut-off assignable to the shadowing of first layer atoms by adjacent first layer atoms (S11). The position of the S11 cut-off was at the proper angle predicted by the scattering potentials previously measured on $\text{Mo}(100)$.¹ The incident angle dependence measured in the $[1\bar{2}1]$ and $[2\bar{1}\bar{1}]$ azimuths

Fig. 8.3. The Li^+ single scattering intensity from clean $\text{Mo}(111)$ is shown as a function of incident angle, ϕ , measured from the surface plane. The dependence is shown for four different total scattering angles.

(60° apart) show pronounced features at incident angles larger than that where S11 is observed (Fig. 8.3), and the features differ between the two azimuths. The features can be attributed to shadowing or blocking. Measurement of the features as a function of total scattering angle allows conclusive differentiation between shadowing from incoming ions and blocking of exiting ions. Consideration of the atomic geometry allows assignment of which atomic layers are contributing. Accurate measurement of the critical angles yields directly the spacing between first and second layers or between first and third layers. In some cases, the proper scattering angle can be chosen to rigorously exclude contributions from all layers deeper than the second or third. Using these methods, the first interlayer spacing is found to be contracted by 18% and the second interlayer spacing is found to be bulk-like or slightly (<4%) expanded.

The phenomenon of surface layer relaxation has been studied by LEED and high energy ion scattering, but these are the first results obtained by low energy ion scattering. Most previous work has been on surfaces in which the stacking sequence repeats every other layer so that first and third layers are in registry. Such systems typically show a contracted first layer and an expanded second layer.⁴ The stacking sequence on bcc(111) surfaces repeats every third layer. Theory has suggested that both first and second layers might be contracted for such a surface.⁵ Previous LEED results on Fe(111)⁴ show a first layer contraction similar in magnitude to the present Mo(111) results, but no information about the second layer spacing was obtained. The present results are the first measurements of second layer spacing for such a system and give no support to the proposed contracted second layer spacing.

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8.2.3 Sulfur Overlayers on Mo(111) (S. H. Overbury)

We have previously studied adsorption and bonding geometry of overlayers of S on Mo(001).¹ Adsorption and surface reactions in general are known to be sensitive to and to affect the structure of the underlying substrate. It is therefore interesting to compare S overlayers on other Mo crystal surfaces, and we have chosen the Mo(111). This open surface has a variety of possible bonding sites of different coordinations and a tendency to facet upon adsorption.

The adsorption of sulfur on Mo(111) has been studied by alkali ion scattering and Auger electron spectroscopy (AES). An electrochemical doser was used to generate S overlayers by S₂ adsorption. Dosing was done at 300-400 K. It is found that larger coverages of S can be deposited on Mo(111) than on Mo(001) under these conditions. Annealing of these high S coverage surfaces at sequentially higher temperatures leads to an abrupt decrease of the surface S coverage at 1050 K, presumably due to desorption. The amount of S remaining is a function of annealing temperature and duration and is independent of previous S coverage. Using AES calibration curves obtained for S on Mo(001), it is believed that the high temperature coverage is equivalent to about a single monolayer (ML), which for a Mo(111) surface is $5.8 \times 10^{14} \text{ cm}^{-2}$. As with Mo(001), the S strongly inhibits adsorption of CO and other ambient gases, making this surface very stable in UHV.

Preliminary Li⁺ scattering measurements have been made from this surface. A strong S single scattering peak is observed at grazing incidence. Similar to the case of Mo(001), this indicates that at least some of the S is above

the level of the first layer Mo atoms, rather than beneath the surface or substituting for Mo atoms. The dependence of the Mo single scattering peak intensity upon incident angle is characterized by prominent shadowing and blocking features for the clean surface. Some of these features are relatively unaffected when 1 ML of S is present, e.g., the S31 and B21 features in Fig. 8.4, suggesting that the surface is essentially unreconstructed. Some features, such as the S21 feature, remain but are shifted somewhat in angle, while other features such as the S11 feature are strongly attenuated. A slight shift can be attributed to an S atom rather than an Mo atom shadowing an Mo atom, and the observed angle will depend upon the S position. A strong attenuation of the shadowing of top layer Mo atoms by other top layer Mo atoms (the S11 feature) is expected by blocking by surface S atoms. At higher coverages of S, all features observed in the $[1\bar{2}1]$ azimuth are strongly attenuated (Fig. 8.4).

Fig. 8.4. The incident angle dependence of Li^+ single scattering from Mo is shown for a clean Mo(111) surface and for the surface with two different coverages of sulfur.

The interpretation of all the observed effects is not yet complete, and some seemingly contradictory results have been obtained. The effects of variations in coverage and long range ordering have not been sufficiently investigated. Analysis by computer simulation as well as the use of multiple scattering analysis in K^+ ion scattering will be brought to bear on the problem. One technical difficulty of acquiring the incident angle dependence will soon be solved by the incorporation of computer controlled stepping motors to scan the relevant angles.

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8.2.4 Surface Studies of Amorphous $\text{Fe}_{80}\text{B}_{20}$ ¹ (D. R. Huntley, S. H. Overbury, D. M. Zehner,¹ and W. E. Brower, Jr.²)

To extend our ion scattering work³ on amorphous and crystalline metallic glasses, we have completed an extensive study of the composition and electronic structure utilizing Auger electron and x-ray photoelectron spectroscopies. Both the rapidly quenched (RQ) and free surface (FS) sides of an amorphous ribbon of $\text{Fe}_{80}\text{B}_{20}$ (Allied Chemical METGLASS 2605) were examined, and essentially no differences were observed between the two sides. The samples were annealed for ~20 hours at 550°C, which crystallized the bulk as verified by x-ray diffraction.

Auger electron spectroscopy was utilized to monitor surface purity. Small amounts of carbon and oxygen were always present on the sputtered surfaces. Annealing results in an increase in the surface carbon and oxygen and in the diffusion of P, S, Cl, Si, C, O, and N to the surface, all of which could be effectively reduced by ion sputtering. Typically, the annealed surfaces were sputter cleaned to reduce the impurities, and then annealed briefly to reduce the sputter damage. The Auger lineshape of the boron peak was strongly

perturbed by the presence of impurities (especially N), so no attempt to determine the surface stoichiometry by the AES intensities was made.

X-ray photoelectron data were obtained for the B 1s, Fe 2p, Fe 3s and Fe 3p core levels for amorphous and crystallized $\text{Fe}_{80}\text{B}_{20}$. The binding energies at the peak maxima were obtained graphically and are reported in Table 8.6. Intensities relative to the Fe 2p $3/2$ are given in Table 8.7. These values were obtained after the subtraction of a smooth background and are corrected for the analyzer transmission function.

The surface stoichiometry was estimated from the integrated areas under the Fe 2p and 3p and the B 1s peaks. Since the peak areas were the same for both sides of the foil and were independent of whether the sample was crystalline or amorphous, sputtered or annealed, an average stoichiometry was calculated. Utilizing empirical sensitivity factors,⁴ a nominal stoichiometry of $\text{Fe}_{85\pm2}\text{B}_{15\pm2}$ was obtained. Using calculated atomic sensitivity factors,⁵ a stoichiometry of $\text{Fe}_{76\pm2}\text{B}_{24\pm2}$ was obtained. These estimated stoichiometries bracket that expected from the bulk composition. In addition, since the Fe/B ratio does not change with sputtering or annealing and the Fe 3s/Fe 2p and Fe 3p/Fe 2p ratios are the same for pure iron and the foils, it seems unlikely that significant segregation or preferential sputtering has occurred.

Table 8.6. XPS core level binding energies^a (eV)

Sample	Fe 2p _{1/2}	Fe 2p _{3/2}	Fe 3s	Fe 3p	B 1s
RQ, sputtered	719.4	706.6	91.1	52.8	187.4
RQ, annealed	719.4	706.4	90.8	52.8	187.8
FS, sputtered	719.4	706.4	90.9	52.8	187.5
FS, annealed	719.4	706.4	90.9	52.7	187.8
Fe foil	719.5	706.4	91.0	52.5	

^aAu 4f_{7/2} = 84.1, all errors are ± 0.1 eV, reported are peak positions.

Table 8.7. Relative intensities^a of XPS core level spectra

Relative Intensities ^a of XPS Core Level Spectra				
Sample	Fe 2p _{1/2}	Fe 2p	Fe 3p	B 1s
RQ, sputtered	0.43	1.4	0.18	0.015
RQ, annealed	0.43	1.4	0.18	0.019
FS, sputtered	0.43	1.4	0.16	0.019
FS, annealed	0.44	1.4	0.16	0.019
Calculated ^b		1.5	0.13	0.016
Fe foil	0.37	1.4	0.18	

^aIntegrated intensities, after background subtraction, relative to the area of the Fe 2p_{3/2} peak. Estimated errors are about 15%.

^bRelative intensities calculated assuming the bulk stoichiometry, $\text{Fe}_{80}\text{B}_{20}$, using the empirical sensitivity factors in Ref. 4.

There were no significant differences in the Fe core level binding energies between the two sides of the foil, or between the crystallized and amorphous phases. The binding energies obtained from the alloys are essentially the same as for pure iron, with the possible exception of the Fe 3p level which is consistently shifted to slightly higher binding energies in the metallic glass. The B 1s core level exhibited a slight shift (0.3-0.4 eV) shift to higher binding energy when the amorphous material was annealed overnight. The peak tended to shift back to lower binding energy when the annealed material was subsequently sputtered. This result suggests that the electronic structure of the B on the sputtered surfaces is independent of whether the bulk is crystalline or amorphous. The binding energy shift induced by crystallization is small and is probably due to structural changes. It is unlikely that significant charge transfer is occurring since no shifts were observed in the iron core levels.

The valence band x-ray photoelectron spectra from the foils are dominated by a major peak at ~ 1 eV which is due to the Fe 3d bands. The energy, shape and width of this band are independent of whether the surfaces were sputtered or annealed, amorphous or crystalline. A

weaker feature was observed at ~ 9 eV in spectra obtained from sputtered surfaces of both the amorphous and crystallized materials and is due primarily to B 2p levels mixing with the Fe 3d bands.

We have applied ion scattering spectroscopy, XPS and AES to amorphous and crystalline Fe₈₀B₂₀. We have observed no differences in atomic scale roughness, composition or electronic structure between the two sides of the foil. Crystallization results in the segregation of several impurities to the surface but does not change the Fe/B ratio. There is no evidence for segregation in either the amorphous or crystalline materials. Crystallization also causes a shift in the B 1s core level which is probably due to structural changes. No corresponding shifts are observed in the iron core levels, suggesting that little or no charge transfer is occurring in these materials. A feature due to B 2p levels was observed in the valence band spectra from sputtered surfaces. The ion scattering results indicated that crystallization did not alter the atomic scale surface roughness, which is in agreement with earlier catalytic measurements.

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8.2.5 Surface Studies by Multi-Charged Ion Scattering

(S. H. Overbury, F. W. Meyer,¹ C. C. Havener,¹ D. M. Zehner,² W. Heiland³)

Preliminary experiments have been conducted to explore the possibility of using multi-charged ions as a probe of surface properties.

It is believed that new information about the processes and mechanisms of surface ion neutralization can be obtained from ion-surface scattering experiments. The multi-charged ions carry large neutralization potential energy which can result in Auger emission from the surface atoms or from the ion. At grazing incidence, a majority of the ions do not penetrate below the top layer, so the resulting Auger emission is determined by the surface electronic states. Experiments which characterized the reflected ion charge state and the secondary electron emission have been reported,^{3,4} but generally such experimental data is limited due to the scarcity of facilities for generating multi-charged ions in this energy range. The present experiment is, to our knowledge, the first study of the energy distributions of secondary electrons produced during multicharged ion-surface collisions.

The experiments were performed at ORNL's electron cyclotron resonance multi-charged ion source. Beams of N⁵⁺, N⁶⁺, O⁶⁺, and O⁷⁺ were produced at 10-kV source potential. After charge selection and beam collimation, the ions were incident at 5° on a Au single crystal mounted in an ultrahigh vacuum chamber equipped with a 4-grid LEED system. The Au surface could be characterized by AES and LEED. The energy distributions of the multi-charged ion induced secondary electrons were obtained by using the LEED grids in the retarding field mode, and numerically differentiating the transmitted secondary electron current with respect to retarding voltage.

The secondary electron spectra observed for N⁶⁺ and O⁷⁺ incident projectiles show two peaks superimposed on a "kinetic emission" background having a monotonic energy dependence. Peaks were observed at ~ 350 eV and ~ 480 eV for N⁶⁺ and O⁷⁺, respectively, and are believed to be associated with Auger decay of the K shell vacancy in the H-like projectile via electrons in highly excited states. These high lying states are populated during the collision by resonance neutralization from the valence and conduction bands of the solid. A lower energy peak at ~ 250 eV occurs for both ions and is

believed to be associated with Auger decay of a Au atom inner shell vacancy created during the collision.

Secondary electron spectra were also measured for N^{5+} and O^{6+} incident projectiles, whose ground state configurations have filled K shells. These spectra were dominated by the "kinetic emission" background. Peaks at 350 eV or 480 eV could be discerned for these ions, but they were greatly reduced in size. The peaks are believed to be due to metastable He-like ions in the beam. Since these metastable ions necessarily have K shell vacancies,

the secondary electrons they produce during surface collisions manifest the same Auger peaks as were observed for the H-like ions.

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9. ELECTRON SPECTROSCOPY

The basis of the photoelectron dynamics of atoms and molecules is being constructed with the aid of angle-resolved photoelectron spectroscopy coupled to synchrotron radiation. Molecular studies have concentrated on (1) autoionization between the spin-orbit split states of HI and (2) the Cooper minimum in the chloromethanes and in the mixed halide, ICl. Work on atomic vapor has included the investigation of the lightly bound electrons in lead, the 4f electrons in ytterbium and the 4d electrons in tin.

9.1 Photoelectron Dynamics of Free Molecules.

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Through the means of angle-resolved photoelectron spectroscopy, coupled to synchrotron radiation, substantial progress has been made during the past year with regard to understanding the fundamental processes in the photoionization of free molecules. A large number of chemical systems have been studied for a wide variety of phenomena. To provide an overall viewpoint Table 9.1 gives a

listing of those studies carried out during the past year. From this list two topics of prime importance have been selected for discussion in this report: autoionization and the Cooper minimum in molecules.

Autoionization in HI. In the photoelectron spectrum of HI, two sharp peaks of nearly equal intensity occur, representing the lowest ionization potentials. They are separated by 0.66 eV and arise from the spin-orbit splitting of the two lone-pair orbitals of iodine. Two lone-pair molecular orbitals in HI ($\pi_{3/2}$, $\pi_{1/2}$) are expected to be highly atomic in character, being derived

Table 9.1. Research done on photoelectron dynamics (Jan 85 - Jan 86)

<u>Molecules</u>	<u>Specific Study</u>	<u>Calculations</u>
CH ₃ Cl	Cooper Minimum	
CH ₂ Cl ₂	Cooper Minimum	
CHCl ₃	Cooper Minimum	
Ethylene	Autoionization	MSX α
N ₂	Autoionization	
HI	Autoionization	
CH ₃ I	Autoionization	
C ₂ H ₅ I	Autoionization	
C ₃ H ₇ I	Autoionization	
I ₂	Cooper Minimum, Shape Resonances, Autoionization	MSX α
ICl	Cooper Minimum, Shape Resonances	MSX α
Ferrocene	Variation of β	
Cr Hexacarbonyl	Variation of β	
Methyl Cyclopentadienyl Mn Tricarbonyl	Variation of β	

from the $5p_{1/2}$ and $5p_{3/2}$ orbitals of iodine. Thus, HI provides atomic type behavior in a molecular environment, which may be studied profitably by theoretical calculations.

Results on the photoelectron cross section and angular distribution parameters, β , of HI leading to the final state $2\pi_{3/2}$, $v = 0$ are shown in Fig. 9.1. over the range of photon energy 10.4 to 11.2 eV. Between these energies lie a series, or rather several series, of Rydberg states converging to the second ionization potential. The nature of these different series has been discussed previously.^{6,7} In analogy to atomic xenon (which is isoelectronic with HI) there is a basic division into two series of broad and sharp resonances.

Fig. 9.1. Cross sections (lower plot) and β values (upper plot) as a function of photon energy in eV for photoionization of hydrogen iodide. The final state is the $2\pi_{3/2}$ ($v = 0$) of HI^+ . The ionization potentials for the $2\pi_{3/2}$ and $2\pi_{1/2}$ states are indicated as well as the energy positions for the first Rydberg series as given in Ref. 7.

Lefebvre-Brion et al.⁶ have made calculations on the cross sections and β values for the autoionization states in HI over a limited photon energy range (10.73 to 10.62 eV). These calculations have been based on the powerful multi-channel quantum defect theory (MQDT), which has been employed thus far in only a few selected cases for molecules. The calculations have been compared with the total photoionization cross section.⁷ Since our data on this photoelectron cross section give similar results, they will not be discussed here, but rather the β values, which have been experimentally determined for the first time, are given in Fig. 9.2. There is no evidence of sharp structure in the experimental β plot due to sharp resonances except for a notch about 10.68 eV. The experimental lack of structure

Fig. 9.2. β values as a function of wave length ($\text{\AA}$) or ionizing radiation. Equivalent values are also given in eV. Final state of the ion is $2\pi_{3/2}$ ($v = 0$) for HI^+ . The experimental data are shown for two different runs at 1.4 $\text{\AA}$ ($\bullet$) and 1.0 $\text{\AA}$ ($\times$). Dashed plot is from MQDT calculations of Lefebvre-Brion et al. (Ref. 6).

is due in part to the finite resolution of about $1 \text{ \AA}$. However, even with improved experimental resolution, it is probable, as evidenced from the experimentally observed resonances in the cross section which are weaker and broader than predicted, that large rapid changes in the experimentally determined β will not match the theoretical calculations. It is more profitable to investigate the changes in β over the broad resonances. The calculated values are lower than experimental at the lower energies and higher at higher energies (see Fig 9.2). However, if we examine the portion of the broad resonance that begins experimentally at about 10.62 eV and is completed at about 10.69 eV, the agreement between experimental and theory is not unreasonable over this region. Namely, β rises quickly from a negative value as one increases the photon energy and then levels off at about a $1/2$ unit of β . Moving the theoretical plot over by $1 \text{ \AA}$ (as suggested earlier with the cross section data), improves the agreement between theory and experiment even more.

The relative intensity of transitions to the excited vibrational states of $^2\pi_{3/2}$ for HI^+ following photoionization is very low in the photon energy regions of resonance. At 21.2 eV for example, the ratio of intensities for $(v = 1)/(v = 0)$ is about $1/30$. This situation drastically changes at a photon energy corresponding to an autoionization resonance. Thus, a similar study to that shown in Fig. 9.1 was carried out in which the first ionic state corresponded to the first excited vibrational state ($v = 1$) rather than the ground state ($v = 0$). A number of resonances were found to feed both the $v = 0$ and $v = 1$ vibrational states but with varying branching ratios. Most interesting is the presence of resonances above the IP for the $^2\pi_{1/2}$ state (11.05 eV). These are not seen or are negligible in the constant ionic state (CIS) run on $^2\pi_{3/2}$ ($v = 0$). They probably result from a Rydberg series to the $^2\pi_{1/2}$ ($v = 1$) ionization

potential (11.31 eV). It has been noted before⁸ in the study on N_2O that Rydberg states going to a vibrationally excited, $v = 1$, state of a higher electronic state will decay by electronic autoionization to the $v = 1$ excited vibrational state of a lower electronic state (i.e., $\Delta v \neq 0$).

In conclusion, although autoionization processes between the lone-pair orbitals of HI bear a close resemblance to atomic processes, molecular effects play an important role. Some of these are reflected in the behavior of the excited vibrational levels and others in the proliferation of new channels to the resonant processes. Thus, the study of the autoionization between the pairs of spin-orbit split states in iodine-containing molecules should offer a valuable avenue for attacking the general problem of the photoelectron dynamics of molecules. Studies of a similar nature should be extended to other molecules containing iodine. Such studies have indeed been initiated on I_2 and the alkyl iodides.

Cooper Minimum for Molecules. When a matrix element describing a given photoelectron process changes sign as a function of photon energy, the transition probability goes to zero. If the given process represents a major channel, the photoelectron cross section will go through a minimum. This phenomenon, well known in atomic physics as a Cooper minimum, has been shown to also occur in molecules, and a number of studies have been carried out on different molecular systems.⁹ In this report, two aspects of how the chemical environment can effect the Cooper minimum are considered from recent results on (1) the chloro methanes and (2) ICl .

A. The Chloro Methanes. One of the first molecules to be studied for its Cooper minimum was CCl_4 .¹⁰ Last year we reported¹¹ on a series of related freons ($\text{CF}_x\text{Cl}_{4-x}$). Most recently we have investigated the analogous chloromethanes ($\text{CH}_x\text{Cl}_{4-x}$). In each case the molecular orbitals undergoing the

most pronounced Cooper minima were the chlorine 3p lone-pair orbitals. However, bonding orbitals containing some 3p character also showed some reduced effect or "partial Cooper minimum." In practice, it has been found more valuable to use the behavior of β as a function of photon energy rather than the cross sections for the criteria of a Cooper minimum. The value of β for a chlorine lone-pair orbital as plotted against photon energy (or photoelectron energy) first rises above +1 and then falls rapidly to zero at a photoelectron energy in the region of 35 eV and then rises again. This behavior of the molecular orbitals resembles closely that of atomic systems (e.g., the 3p subshell of argon or chlorine). Fig. 9.3 shows the results of β for the three outer valence orbitals of CH_3Cl . The 3e orbital yields at the minimum a β value of +0.3; a slight dip is found for the 7a, obtained at about the same energy with a β value of +0.8, while no evidence of effects of a Cooper minimum are seen with the 2e orbital. Using CNDO calculations it has been possible to estimate the partial electron density of the different orbitals in terms of the percent contribution of the chlorine 3p subshell. For example, calculations on CH_3Cl suggest a contribution of 91%, 42% and 5% respectively for the 3e, 7a, and 2e orbitals. An argument is made that the larger the 3p character of the orbital, the larger the effect of the Cooper minimum. This correlation has worked well for all the chloromethanes in separating the orbitals into three main categories: mostly Cl3p character, partly Cl3p character, and very little Cl3p character. However, a more detailed comparison shows frequent discrepancies. It is hoped that more sophisticated approaches may improve the correlation between the Cooper minimum effects and the nature of the molecular orbital.

8. ICl. The position of the minimum in β for the lone pair orbital in Cl_2 is 32 eV in photoelectron energy and for I_2 is 43 eV. It is interesting to consider with a mixed

Fig. 9.3. Experimental β values are plotted against photon energy ($h\nu$) for the outer three valence orbitals of CH_3Cl . Solid lines are drawn for aid in the discussion. The ionization potential is indicated for each orbital. The photon energy is equal to $h\nu - \text{IP}$. Closed circles based on data taken with toroidal grating monochromator; open circles are from data using Seya monochromator.

halide, such as ICl , how the lone-pair orbital will affect the energy position of the minima. Calculations on ICl as well as I_2 and Cl_2 using the multiple scattering X_α method reveal that the minimum of β for the 2π orbital of ICl (which is assigned to the lone pair of Isp) lies midway between the minimum values of β for the lone-pair orbitals from I_2 and Cl_2 . This is confirmed by experimental results which give 37 eV.

In conclusion, the Cooper minimum in molecules is an important phenomenon in photoelectron dynamics which deserves study in itself. In addition, investigation of the effects of the Cooper minimum, particularly the β values, provide a means for characterizing the nature of molecular orbitals, at least for those orbitals that are strongly derived from atomic orbitals that can undergo Cooper minima.

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9.2 Photoeffect as a Probe of Atomic Structure and Dynamics

(M. O. Krause, P. Gerard¹, A. Svensson², T. A. Carlson)

During the past few years we have demonstrated the efficacy of the photoeffect to

elucidate the electronic structure and dynamics of atoms. If the photons are taken from a synchrotron radiation source, as we do in our work, a wide energy range can be covered continuously and the dynamic behavior of the bound electrons, including electron correlation, and the photon-electron interaction can be examined in great detail. Using an electron spectrometer system developed at ORNL, we have measured the partial photoionization cross sections and the angular distribution of the ejected photoelectrons and have obtained during the previous periods detailed information on the ionization of p and d electrons of various metal vapor atoms, on two-electron processes that give rise to correlation satellites in the photoelectron spectra, and on autoionization resonances in open-shell atoms. Work during the present period was directed toward (a) establishing the dynamical properties of the 4f electrons in ytterbium, (b) delineating the properties of the lightly bound electrons in lead, the heaviest stable element that can be readily studied as a monoatomic vapor, and (c) determining the cross section and the β angular distribution parameter for the 4d electrons in the tin atom.

9.2.1 Photoelectron Studies of f Electrons: The Missing Link

We finalized the study of the 4f electrons of Yb in a collaborative effort with theoreticians at the University of Notre Dame. The major goal of this work³ was to probe the potential of the most sophisticated theory to date, the relativistic random phase approximation (RRPA), to properly describe the f electrons and their transitions under the influence of electromagnetic radiation. Previously, this theory had been shown to make realistic predictions for the p and d electrons, and with some exceptions, for the s electrons, but no definitive test had been made for the f electrons. Now, our study of the 4f electrons of Yb has clearly demonstrated that the RRPA model accurately predicts the photoionization cross section and the β parameter (two of the important dynamical properties) also for the 4f

electrons, thus providing the missing link to a complete description of all the electrons in their ground state and their transitions to the continuum. This result is significant because it proves that the RRPA theory accounts for the relativistic effects and especially the dominant electron correlation effects in all electronic subshells of the atom. We must note, however, that the ensuing deeper understanding of the electronic structure and dynamics is, at the present limited to closed-shell atoms, such as the rare gases, Pd, Yb, and the group II-B elements. Nevertheless, the knowledge gained from the study of the closed-shell atoms can now be applied judiciously to open-shell atoms and used in the future for guidance in experimental and theoretical studies of the open-shell atoms, which constitute about 70% of the elements in the periodic table.

9.2.2 Studies of a Heavy Element: The Pb Atom.

Lead is the heaviest stable element that can readily be obtained as a monoatomic vapor. It has the nominal open-shell configuration $5d^{10}6s^26p^2$, which leads to spectacular effects in photoexcitation because of the possibility of the discrete transitions $6s \rightarrow 6p$ and $5d \rightarrow 6p$. These transitions between energetically close-lying levels are strong and the resulting $5d^{10}6s6p^3$ and $5d^96s^26p^3$ configurations undergo rapid autoionization into the various available continuum channels. Relativistic and electron correlation effects lead to a great many multiplet levels in both the initial and final states as well as the intermediate states that are considered in the autoionization processes. The resulting photoelectron and Auger electron spectra can be quite complex as seen in Fig. 9.4. Similarly, the autoionization structures which we resolve into the various exit or decay channels can be equally complex as shown earlier for the $6s \rightarrow 6p$ resonances.⁴

We have now completed a survey study of Pb ranging from the ionization threshold at 7.4

Fig. 9.4. Electron spectrum of atomic Pb showing the 6p, 6s and 5d photoelectron lines and the Auger lines that follow 5d ionization. Only the major lines of the complex multiplets are designated. Because there is only one final two-hole state ($6p^2$), the Auger spectrum is the mirror image of the 5d multiplet. Spectrum is not corrected for the transmission of the analyzer.

eV to 110 eV. Both the partial cross sections (σ) and the β parameters were measured for the 5d, 6s and 6p subshells. Generally, the multiplet structure could be resolved at the low photon energies, but due to the multitude of lines, many of them weak, we restricted our studies to the major components only.

As an example, we describe the results for σ of the $5d_{5/2}$ and $5d_{3/2}$ components, while a more detailed discussion is given in a forthcoming paper.⁵ Fig 9.5 shows our results in the region between 30 and 110 eV, where no autoionization resonances occur. As characteristic for d electrons, $\sigma(5d)$ has a low value near threshold and rises to a broad maximum before monotonically dropping off toward higher energies. The so-called delayed maximum in σ is caused by a centrifugal barrier acting on the d electrons. Because height and width of the barrier are sensitive to the atomic potential chosen, the experimental data offer a good test for the various theoretical models. The figure shows

Fig. 9.5. The partial photoionization cross section of Pb are given as the 5d subshell ($\bullet$) and the $5d_{3/2}$ ($\square$) and $5d_{5/2}$ ($\circ$) components. Data are compared with the results of the single-particle Dirac-Slater (DS) calculation for Pb ($Z = 82$) and the relativistic random phase approximation (RRPA) calculation for Hg ($Z = 80$). For details, see Ref. 5.

that the single-particle relativistic Dirac-Slater (DS) model gives a semi-quantitative account of the observation. However, no RRPA calculations have been reported so far for Pb. Hence, we compare our experimental data with the RRPA calculations that have been made for the nearby element Hg. These Hg predictions are plotted in Fig. 9.5 and a good agreement is seen to exist between Hg - RRPA results and the Pb data. As for $\sigma(5d)$, we find the Hg - RRPA calculations for $\beta(5d)$ in satisfactory agreement with experiment. We also note that the DS results for Pb are quite realistic in the case of the $\beta(5d)$

parameter despite the simplicity of the model.

9.2.3 The 4d Electrons in Sn.

The study of Sn is a natural extension of our studies of Ag⁶ and Pb,⁵ since tin adds (a) another element in the investigation of the 4d electrons and (b) another element within the IV-B group. We measured σ and β for the 4d subshell between 30 and 100 eV and found an intermediate behavior between the data for Ag and the literature values for Xe. In analogy to Pb and Hg, the RRPA predictions for the corresponding II-B element Cd with its closed shell structure are in satisfactory agreement with the experimental data for Sn.

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10. NUCLEAR WASTE CHEMISTRY

Several research topics in the Chemistry Division are directly related to chemical problems of high-level radioactive waste disposal. Safety analyses of radioactive waste disposal depend upon reliable prediction of radionuclide migration in the event of penetration of the nuclear waste repository by groundwater and flow of the groundwater to the accessible environment. Prediction of the migration rates of nuclides within host geological formations is dependent upon knowledge of sorption properties and chemical speciation of the nuclides. In Sections 10.1, 10.2, and 10.5, programs are described for evaluation of the parameters affecting the sorption of Tc, Np, U, Sr, and Cs. Knowledge of the solubilities of nuclides, especially for reducing repository environments, is necessary for prediction of maximum concentrations of nuclides in the groundwaters. In Section 10.3 solubility studies of Tc(IV) oxides are summarized. In Section 10.4, other types of chemical support for assessment and evaluation activities are presented.

10.1 An Evaluation of Retardation Parameters for Nuclide Migration in Geological Media

(R. E. Meyer, W. D. Arnold, J. G. Blencoe, F. I. Case, J. F. Land)

The objective for this program is to evaluate for the U. S. Nuclear Regulatory Commission critical retardation parameters given by the site contractors of the Department of Energy with respect to their adequacy and pertinence in high-level waste repository safety assessment. In the event of a breach of a repository by groundwater, the nuclides may be mobilized and transported to the environment. Safety analyses must demonstrate that the quantity of nuclides released from the repository and transported must be maintained within acceptable limits. Particular emphasis has been given to sorption of technetium, neptunium, and uranium on various samples of crushed basalt of the types found at the Hanford, Washington, proposed site for high-level waste. Recently, studies have been initiated for study of sorption on tuff samples from the Yucca Mountain proposed site in Nevada for a high-level waste repository.

During the past year, experiments have included studies of sorption of technetium, neptunium, and uranium onto samples of Cohasset basalt, the type basalt which is currently the horizon selected for the proposed repository in Hanford, Washington. Significant sorption of technetium and neptunium was observed under anoxic conditions if

great care was taken to eliminate traces of oxygen from the synthetic groundwaters used in the experiments. The behavior of uranium in these synthetic groundwaters was dominated by the formation of sodium boltwoodite, $\text{Na}(\text{UO}_2)(\text{SiO}_3)(\text{OH}) \cdot 5/2\text{H}_2\text{O}$. This solid formed slowly with time in solutions of synthetic groundwaters maintained at 60°C, the ambient temperature of the basalt formation.

These results are compared to those of the DOE projects for the candidate repository sites. Details of these experiments and comparisons are presented in NUREG annual and quarterly reports.¹⁻⁴

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10.2 Sorption of Tc on Basalt

(W. D. Arnold, R. E. Meyer, F. I. Case)

Technetium is only slightly adsorbed onto basalt under oxic conditions,¹ and it is adsorbed onto basalt under anoxic conditions only if extreme care is taken to remove all oxygen from the groundwater/basalt system^{2,3} or if reducing agents are present in the groundwater.⁴ In addition, the basalt must be ground and stored in an oxygen-free environment if significant sorption is to be observed. The mechanism by which technetium is adsorbed onto basalt appears to be quite complex and is not understood. To further understand this process, experiments on the stability of technetium in groundwaters and on the aging of basalt and groundwaters are being carried out. These experiments include analyses of groundwater in contact with basalt along with analyses of the technetium content of the groundwaters. Aging of the basalt in deoxygenated groundwater for 60 days did not appear to affect the sorption reaction. Significant increases in sorption were observed when basalt that had been pre-equilibrated with groundwater was contacted with fresh groundwater that had not been pre-equilibrated with basalt. Details of the experiments on the sorption of technetium are published in NUREG reports.^{3,5}

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10.3 Solubility Studies of Tc(IV) Oxides

(R. E. Meyer, W. D. Arnold, F. I. Case, J. F. Land)

Based upon current knowledge of technetium chemistry, it is generally predicted that some form of Tc(IV) oxide would be formed if reducing conditions exist in a repository environment and Tc is released from the stored waste by a groundwater-intrusion event. The solubility of Tc(IV) oxides is one of the parameters necessary for the calculation of the transport rate of technetium for the case of solubility-limited transport. However, technetium has an unusually complicated redox chemistry, and much is unknown about the chemistry of reduced valence states of technetium. In particular, little is known about the solubilities of Tc(IV) oxides. The solubility of technetium (IV) oxides was therefore determined in solutions of NaCl, HCl, and synthetic basalt groundwaters in the pH range 0 to 10.

The technetium (IV) oxides were prepared either by electroreduction from Tc(VII) solutions onto platinum electrodes or by precipitation of Tc from Tc(VII) solutions using hydrazine. In some of the determinations, the oxide was precipitated onto purified sand by use of hydrazine. The oxide-covered sand was

then placed into a column and the test solution continuously recirculated through the column. The oxide plated on platinum was placed into a small cell and the test solution stirred. Solubilities were determined by measuring the beta radiation of ^{99}Tc in the stirred or circulated solution in contact with the oxide. In the pH range 4 to 10, solubilities were in the range 7.5×10^{-9} to 5×10^{-8} mol/L, and most of the determinations were in the range 1×10^{-8} to 2×10^{-8} mol/L. In acid solutions the solubilities were generally higher for hydrazine-precipitated oxide than for the electrodeposited oxide, and they increased as the pH was lowered. Solubilities of Tc(IV) oxides will be useful for calculation of transport rates of technetium for the case of solubility-limited transport in nuclear waste repository environments. Details of these measurements have been published in a NUREG report.¹

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10.4 Review and Evaluation of Literature on Geochemical Issues Pertinent to the Disposal of High-Level Radioactive Wastes: Technical Assistance to Geotechnical Staff of the Nuclear Regulatory Commission

(J. G. Blencoe)

The Department of Energy (DOE), the Nuclear Regulatory Commission (NRC), and the Environmental Protection Agency (EPA) are currently spearheading a national program to develop a safe method for disposal of high-level radioactive wastes (HLW). The DOE has determined that research and development activities related to this effort should be concentrated on testing the feasibility of using mined geologic repositories as hosts for the wastes. The idea behind this approach is that a combination of man-made and natural

barriers will isolate the wastes so that they will never pose a threat to the public.

The Nuclear Waste Policy Act of 1982 (Public Law 97-425) formally defines the individual responsibilities of the DOE, NRC, and EPA in effecting the disposal of civilian (commercial) HLW. The EPA is responsible for developing "... generally applicable standards for protection of the general environment from offsite releases from radioactive materials in repositories." The NRC is responsible for implementing the EPA standards, and also must develop and issue "... technical requirements and criteria that it will apply in approving or disapproving (i) applications for authorization to construct repositories; (ii) applications for licenses to receive and possess spent nuclear fuel and high-level radioactive waste in such repositories; and (iii) applications for authorization for closure and decommissioning such repositories." The DOE is responsible for collecting the data needed for site characterization, and for constructing and operating a repository in accordance with NRC regulations.

Most of the natural barriers to radionuclide migration from an HLW repository are geochemical in nature. For example, although groundwater is the likely vehicle by which radionuclides can be transported from a repository, it is also true that only small amounts of radionuclides will dissolve in groundwater. Consequently, the low solubilities of radionuclides in groundwater can be viewed as an important barrier to radionuclide migration. Other geochemical barriers to radionuclide migration include sorption of dissolved radionuclides by minerals in the rocks through which radionuclide-bearing groundwaters travel, and diffusion of radionuclides into the more-or-less static groundwater which occupies the pore spaces of rocks adjacent to radionuclide-release pathways (aquifers). These various examples of geochemical barriers to radionuclide migration illustrate why the performance of a proposed

repository cannot be predicted satisfactorily without an extensive body of information concerning geochemical conditions that are anticipated to exist in and around the repository after it has been constructed and radioactive wastes have been emplaced.

The overall purpose of the technical assistance project is to aid NRC geochemistry personnel in determining what additional geochemical information about a candidate-repository site is required prior to the time that the NRC must decide whether or not to issue a license to construct the repository. More specifically, it is the responsibility of project staff members to provide technical assistance to the NRC by performing the following tasks: (1) compile and assess all of the available geochemical data for candidate-repository sites, (2) evaluate extant DOE programs for determining the geochemical characteristics of potential repository sites, (3) review and appraise reports, journal articles, and the parts of DOE site-characterization plans that deal with geochemical issues, and (4) review draft technical material written by NRC geochemistry personnel for inclusion in NRC documents. The results of these various activities are usually transmitted to the NRC in the form of reports that identify and attempt to resolve particular geochemical issues and concerns. Examples of documents written for the project include "topical review" papers on the solubility and sorption of radionuclides in basalt-groundwater and tuff-groundwater systems, and reviews of numerous reports and journal articles that deal with issues pertinent to the candidate-repository sites at Hanford, Washington, and the Nevada Test Site.

Project staff also have the responsibility to attend meetings, symposia, workshops, etc. that deal with geochemical aspects of the disposal

of high-level radioactive wastes. After attending such a meeting, a staff member must prepare a trip report in which he outlines the agenda of the meeting, the most important new information that was presented at the meeting, and his general impressions of the usefulness of the meeting. This trip report is then sent to the NRC staff for their examination and evaluation. This year various staff members attended approximately five different meetings that dealt partly or entirely with geochemical issues related to the disposal of high-level radioactive wastes.

10.5 Sorption of Radionuclides on Clays and Shales

(P. C. Ho, W. D. Arnold, R. E. Meyer)

The Sedimentary Rock Program (SERP) is investigating shales in the United States for their potential suitability as host rocks for the disposal of high-level radioactive waste. In support of this program, preliminary scoping studies were carried out of sorption of U, Tc, Sr, and Cs on montmorillonite and illite, clays common to shale formations. A synthetic groundwater made up to simulate highly saline groundwaters in the Conasauga shale formations was used under oxic (air present) conditions. Uranium was strongly adsorbed, and technetium was not adsorbed on these clay minerals under these conditions. Cesium and strontium were only slightly adsorbed from the concentrated saline groundwater, but were more strongly adsorbed from dilutions of the saline groundwaters. In addition work has been initiated for study of sorption on a number of shale samples from formations located throughout the United States. These data will be used to help select the potentially most favorable shales for detailed site-specific characterization from among those currently being considered.

11. HEURISTIC MODELING

In the teaching profession, the adjective "heuristic" designates an educational method by which a pupil is stimulated to make his or her own investigations and discoveries. The term heuristic modeling as applied to computational chemistry denotes the application of programming techniques, often from the field of artificial intelligence, to problems in chemistry which are not sufficiently well understood to permit rigorous mathematical modeling and first principle calculations. The diverse areas described below -- printing ink formulation, machine inspection of printed currency, photographic color reproduction, and the synthesis of organic molecules -- require heuristic modeling with a combination of nonnumerical and numerical programming methods.

11.1 Heuristic Modeling

11.1.1 Printing Ink Chemistry and Technology¹

(C. K. Johnson, M. N. Burnett², B. K. Williams²)

Last year's annual report³ described our initial work on INKY, an expert system for printing ink chemistry. That project for the Bureau of Engraving and Printing (BEP) continues in parallel with a new BEP-ORNL research project described in an accompanying report.⁴

Our systems analysis of BEP ink chemistry and technology yielded a systematic approach to computer-aided formulation based on color and printability concepts, plus knowledge bases and data bases on presses, printed products, ink formulas, and ink components; thus, the three major factors in the INKY system are color, printability, and history. The color aspect was the most susceptible to analytical solution and occupied much of our attention during the past year. We are now proceeding to formulate and test analytical models for the printability aspects of ink formulation. An AI-based heuristic reasoning system will combine the three components on an integrated ink formulation workstation including an on-line reflectance spectrometer for color measurements.

Color characterization for an ink film on a paper substrate is made by measuring the visible reflectance spectrum and transforming it into tristimulus values. Multilayer Kubelka-Munk theory⁵ is then used to obtain the equivalent tristimulus values for an infinitely thick ink film. These values may then be transformed to a 3-dimensional psychometric coordinate system such as the CIE L*a*b* color

space.⁶ A stereoscopic illustration (Figure 11.1) drawn with the ORTEP program,⁷ originally written for crystallographic drawings, illustrates the advantage of using 3-D drawings to depict geometrical relationships in the L*a*b* color space. Extensive experimental testing of the Kubelka-Munk theory was carried out to validate its application to semi-transparent ink film specimens.

Several theoretical methods were derived and tested for the measurement of fractional ink coverage in complex patterns such as those on currency. The simplest and most reliable of these can utilize either transmittance or multiple reflectance measurements with black and white backings. One of the complexities with specimens having fractional ink coverage is the lateral scattering within the paper substrate whereas only vertical scattering is included in Kubelka-Munk theory. Depending on the detailed geometry of the inked pattern and the scattering spread characteristics of the substrate, varying amounts of radiation which are incumbent upon the uninked fractions of the specimen will reemerge in an inked section.

Instrumental measurements of the reflectance spectrum and mathematical interpretation of the results with Kubelka-Munk theory provide a practical model for formulating the pigment composition and adjusting the actual ink color. This eliminates much of the empirical color adjustment heuristics which are very messy to implement with AI methods.

The second ink formulation factor, printability, is less susceptible to a complete analytical solution. The complexity of the heuristics required in ad hoc printability formulation is

Fig. 11.1. Stereoscopic drawing illustrating the color space positions and metameric properties of several pigments in the BEP inventory. The colors red, yellow, green, and blue are found along the $+x$, $+y$, $-x$, and $-y$ axes, respectively. Lightness is indicated along the axis perpendicular to the page with black in the plane of the paper and white coming forward. Each triangle of three points represents one pigment. The large, medium, and small circles represent the apparent colors of the pigment under daylight, incandescent, and fluorescent illumination, respectively. The enclosing polyhedron represents the approximate color space bounds accessible with linear combinations of the BEP pigments.

high, and we find it desirable to reduce as much of the problem as possible to analytical form. Rheological measurements provide the classical experimental characterization for ink, but the statistical correlations between the rheological measurement and the printability behavior, as measured through spoilage statistics, is rather discouraging. Consequently, we have chosen to examine more fundamental physical chemical properties in the hope of finding more robust characterization parameters for use in formulation reasoning.

The CRC Handbook of Solubility Parameters and Other Cohesion Parameters⁸ tabulates and discusses various physical-chemical characterizations which may be applied to the dispersion of colloidal particles such as pigments in ink and paint. There are single parameter formulations with Hildebrand solubility terms or hydrophilic-lipophilic balance terms; a tri-parameter formulation utilizing the three Hansen parameters for non-polar, polar, and hydrogen-bond interactions; and higher multi-parameter formulations which include additional factors such as Lewis acid/base terms. We are currently exploring the relevance of Hansen

parameters to the ink printability problem. We are also exploring an electrochemical experimental approach involving ultrasonics to measure effects related to the zeta potential⁹ on the pigment particles.

1. Research sponsored by the Bureau of Engraving and Printing under interagency agreement with the Department of Energy.
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11.1.2 Automatic Web Currency Inspection System¹

(C. K. Johnson, R. E. Sherrod,² C. A. Goodman²)

The twelve billion or so U.S. banknotes in circulation have life expectancies of 1.5 to 10 years depending upon denomination. Each note is inspected for printing flaws by currency examiners before circulation. This manual examination is effective but costly and does not provide on-press feedback for real-time minimization of currency spoilage (i.e., rejects). The Bureau of Engraving and Printing (BEP) will have a new high volume currency press capable of two-sided tricolor intaglio printing on a continuous web of paper in operation by 1990. Four or five such web presses could replace the 20-30 sheet-fed presses currently used for currency production. Automated on-line inspection using machine vision is planned for the web currency press, and we are working with BEP to develop specifications for the inspection system.

Although paper defects cause some spoilage, most currency flaws are due to excess ink where it should not be or no ink where it should be. A colorful currency examiner's language has evolved describing flaws in terms of location, cause, and shape with nomenclature such as slywipe (slightly wiped plate), stain, mash, board break, setoff, etc.

The simplistic machine approach of subtracting the gray scale pixel representation of the reference image from the test note image and checking threshold tolerances on the difference is inadequate because it does not include consideration of the psychological aspects of

currency flaw perception. Furthermore, fixed thresholds are unrealistic in a manufacturing environment where production schedules might require that a certain systematic discrepancy be allowed until corrective measures are feasible.

We are deriving a flaw specification language to provide a flexible interface between the machine inspection system and the quality control supervisor and press operator. The flaw specification control system will include (1) a causal network relating flaws to their origin on the press, (2) a perceptual network relating the flaw characteristics to the psychological perception characteristics in that region of the note, and (3) an image-decomposition network relating the measurable quantities to flaw characteristic signatures. The causal network requires a detailed analysis of the new press design and the flaw characteristics of related presses. The perceptual network requires a human factor analysis of flaw noticeability and the psychological principles of camouflage and gestalt perception. Parts of the note design tend to hide certain flaws while other parts accentuate certain flaws. On a \$5 bill, for example, a blemish on Abraham Lincoln's eye is noticed immediately, but the often extensive setoff (i.e., ink transfer from the back of one note onto the front of the next note) within the large corner numeral "5" on the front of the bill usually goes unnoticed.

Other subtasks in this research project include organization of a conference on automatic inspection in graphic arts printing and simulation of the complete inspection system and its process control interface. Additional staff members from ORNL and the University of Tennessee will be working with us on this project during the coming year.

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1. Research sponsored by the Bureau of Engraving and Printing under interagency agreement with the Department of Energy.
 2. Department of Chemistry, University of Tennessee, Knoxville.

11.1.3 Nonphotogenic Pigments¹

(C. K. Johnson, M. N. Burnett², and L. A. Boatner³)

The rare earth compound praseodymium orthophosphate (PrPO_4) prepared in a systematic crystallization of the lanthanum orthophosphate series⁴ produced millimeter sized monoclinic crystals with a weak, medium green color characteristic of many praseodymium compounds. However, photographs of the crystals taken with various Kodak and Polaroid films invariably reproduced the green color as bright yellow. This striking color reproduction discrepancy was of considerable concern to the ORNL photographic section, which processes hundreds of photographs each month with systematic procedures for ensuring faithful color reproduction.

Our interest in the effect was the possible application of "nonphotogenic pigments" in inks for counterfeit deterrence since the upcoming generation of color copiers presents a significant threat as a tool for amateur currency counterfeiters. The color reproduction of the PrPO_4 crystals was less discrepant on the Xerox 6500 and Canon color copiers currently available than it was on the photographs. With the Xerox reproduction, the color was too green and with the Canon, too yellow. PrPO_4 has insufficient color strength to serve as a pigment, but scientific curiosity compelled us to trace the origin of the effect.

We did a literature survey to see if other examples of photographic color discrepancy had been reported. Our basic finding was that color photography is a surprisingly unfaithful color reproduction technology and that one should be amazed that commercial color film works as well as it does. The PrPO_4 situation is a striking example of the general phenomenon of nonphotogenic pigments but not necessarily an extreme example. Color copiers also have their physical limitations which may be quite different from those in photographic film.

Ohta^{5,6} shows that the photographic dye spectral sensitivities used in color photography may be selected based on a delicate compromise between photographic color mismatches and the desaturation of reproduced

colors. It is well known that photographers like vivid colors, and one must conclude that the commercial compromise is weighted heavily by that factor.

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2. Department of Chemistry, University of Tennessee, Knoxville.
3. Solid State Division, ORNL.
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11.2 An Expert System for Planning Chemical Syntheses in the Forward and Reverse Directions (William E. Thiessen, John D. Allen, Jr.¹)

We have described in previous reports some early steps in the development of an Expert System for discovering novel synthesis methods for large organic molecules. In those reports, we discussed the varieties of chemical knowledge with which we had endowed the program and the general problem-solving strategies by which the program applied its knowledge to the discovery of a method for synthesizing a specified molecule. We may not have stressed with sufficient vigor that the program should in no way be viewed as a "data-base" system. Its capabilities do not depend upon an ability to recall and string together stored reactions, but rather upon its capacity to apply general synthetic principles to whatever problem is given. It is the refining of this capability which provided the focus for the last year's research.

The intelligent use of any body of knowledge, whether by man or by machine, depends heavily upon a capacity to rule out of consideration very rapidly the application of inappropriate methods. For our chemistry program, this capacity had to a large degree been incorporated in a simple set of constraints on such parameters as target site complexity, number of likely precursors, number of carbon-carbon bonds formed, and the like. Although the extent to which such simple considerations as these can lead to plausible syntheses is frequently surprising, they do not capture enough chemical sense to be generally trustworthy (as one or two dismally unsuccessful generated syntheses will attest). It was clear that, to be more nearly chemically sound, the program would have to be made capable of understanding the global as well as the local nature of the molecular environment with which it was currently concerned and to use its understanding to make better choices about the method and point of attack. It should, for example, emulate the chemist who would know at once that a Grignard reagent cannot be formed from a molecule containing an acidic hydrogen, or that, in general, Robinson annelation could not be undertaken if there were a carbonyl group in the molecule other than those used to form the cyclohexenone structure. More important still, the program should understand when a constraint was not absolute so that it could, for example, mimic the action of the human chemist who would surely recall that there is a symmetry related exception to the Robinson annelation rule involving equivalence of two carbonyls. The program, like the human, should know how to take advantage of the pertinent symmetry when it appeared.

Although we have now succeeded in giving the program the ability to incorporate and utilize knowledge of these and related kinds, it could still blunder badly at times if it had to rely only upon constraints applicable to the structure to be synthesized. Because the program has only a limited "visual" capability, it cannot anticipate every result of invoking a

selected reaction. Thus, there are reactions which the program might find perfectly acceptable which could nevertheless not be carried out because of some condition(s) on the precursor(s). As an example, it could be the case that for some reaction involving the condensation of two precursors, each precursor must have an attached amine group. The human chemist's visual comprehension of the overall molecular structure would provide the insight necessary to decide against attempting the reaction when doing so would not produce the required distribution of functionalities in the precursors. Similarly, a frequently useful heuristic involving multiple precursors is that the precursors, at least those which must themselves be synthesized, should be of approximately equal size. Again, the human's visual sense provides the required insight. The program, running, as it does, backwards, can know nothing of the distribution of atoms and functionalities in the precursors until it carried out the reaction transformations and forms them. Thus, we let the program do exactly that. It makes its best selection of reactions subject to constraints it can apply in the parent molecular structure, generates the precursor(s), and, before it continues, examines the precursor(s) for those constraints which might have rendered the reaction inapplicable. If such constraints are discovered, the program reverses the steps taken to generate the precursors and attempts to find a suitable alternative reaction in the reconstructed parent. Failing this, it backtracks further until a point is found in the so far developed synthesis scheme from which continuation is possible.

It is the ease with which it proved possible to make the program backtrack that prompted consideration of using a reversed version to search for methods for converting hazardous chemical waste materials into non-toxic and useful reagents. Although the reversed version is running and has already discovered a potentially useful conversion scheme for the polymer, polyvinyl alcohol, the program is far

from complete. Of the bodies of knowledge to be added, perhaps the most important is one which will help to ensure that at every reaction step the toxicity of a product is less than that of its precursor or precursors. Of particular economic importance will be a collection of heuristics which will guide the conversion process toward desired end products, or at least toward end products of specific

chemical properties. Thus, the program's user will be able to exercise a degree of control over the conversion methodology which the program employs. It is the discovery of the extent to which the mechanisms for this control can be implemented that will occupy much of our time for the next year.

1. Consultant, I&C Division.

12. SPECIAL TOPICS

12.1 Conservation Programs

The work summarized in sections 12.1.1 and 12.1.2 provides physico-chemical support to programs in the Engineering Technology Division and in the Energy Division. These programs are sponsored by the Department of Energy programs in Thermal Energy Storage through the Office of Energy Storage and Distribution, and in Chemical Heat Pumps through the Office of Industrial Programs, respectively. The Thermal Energy Storage Program is managed by Oak Ridge National Laboratory, and has as its objectives the identification and development of thermal storage technologies which, when implemented, will increase the efficiency of heating and cooling systems for buildings or provide a mechanism for use of waste energy in industrial processes. Efforts in the Chemistry Division include a program related to proposed recovery and storage of thermal energy at high temperatures (650°C) using the enthalpy of fusion of encapsulated phase-change materials. Of particular interest is silicon-encapsulated spheres of aluminum-silicon eutectic. The Chemical Heat Pump Program has as its aim the recovery of waste heat at intermediate temperatures in industrial processes by means of heat pumps driven by chemical reactions (CHP) or by sorption/desorption processes (AHP). Consultation is provided on solution thermodynamics and thermochemistry for use in the identification of fluid pairs capable of providing higher coefficients of performance at higher temperatures than those in use currently (e.g., $H_2O - LiBr$, $NH_3 - H_2O$) can provide.

The work summarized in section 12.1.3 is supported by Energy Conversion and Utilization Technology to develop a body of knowledge on the physical, chemical, and combustion properties of microemulsion fuels using small-angle neutron and x-ray scattering, dynamic light scattering, electron microscopy, and analytical chemistry to provide correlations between combustion and physical-chemical properties. This project is a bridge between basic and applied

research designed to shorten the time required for industry to field microemulsion fuels technologies directed toward emissions reduction and fuel extension with renewables. As such, research encompasses basic aspects, including improved mathematical treatments of scattering data, model systems which form a stepping stone between basic research and applied systems, and phase and scattering studies of practical fuel systems.

12.1.1 Hypereutectic Heat Storage Alloy

(M. R. Bennett, J. Braunstein)

Silicon encapsulated shot of Al-Si eutectic are an attractive possibility for use in direct contact, phase change, heat storage.^{1,2} In evaluating their potential, a key question is the following: "Will an integral silicon shell remain structurally stable during repeated cycling of the shot through the eutectic temperature?" The Al-Si phase diagram indicates that, provided the upper temperature of the cycle is sufficiently far from the liquidus temperature, the equilibrium ratio of solid silicon to liquid alloy is high enough so that the average shell thickness could retain the liquid alloy. However, the question of stability arises from several factors. One is the mechanical strength of the shell subjected to the stress imposed by volume expansion of the alloy on melting. It may be possible to compensate for this by increasing the shell thickness or by the incorporation of voids. A perhaps more fundamental factor is the stability of the silicon shell to redistribution during repeated melting and crystallization, which could lead to disintegration. A number of mechanisms could provide the driving force for such redistribution. These include:

1. A temperature gradient in a fixed direction across a shot, which, even though small, could lead to preferential deposition of Si crystals on the cool side, with thinning of the shell on the hot side.

2. Dendritic growth of primary silicon crystals from supercooled liquid, which could lead to entrapment of alloy and migration of aluminum from the interior of the shot to the surface.
3. The relatively high diffusion coefficient of silicon in aluminum, which provides a path, even isothermally in the solid state, for interdiffusion of silicon and aluminum, with gradual redistribution.³⁻⁵

Thus, although the equilibrium phase relationships show the possibility of an integral silicon shell, the equilibrium is dynamic, not static, and the distribution of the silicon and aluminum phases must be considered.

An experiment has been initiated to test the integrity of silicon shells as containers for Al-Si eutectic.⁶ It is intended to be independent of methods used to fabricate self-encapsulated shot, and to provide basic information on the inherent stability of Si, in contact with Al-Si eutectic, to migration under conditions of temperature cycling through the eutectic temperature but below the hypereutectic liquidus temperature.

Polycrystalline shapes such as plates, rods (or cups) will be immersed in (or filled with) Al-Si eutectic, maintained at temperatures between 550 and 650°C, and subjected to physical and metallographic examination for dimensional stability. Two sets of cycling conditions are planned. One set is the temperature cycling of the samples between 550 and 650°. In the second set, the samples will be maintained at various nearly-constant temperatures between the eutectic temperature (577°C) and 650°C before examination. The latter, isothermal, experiments would measure the inherent rate of redistribution of silicon and alloy resulting from the dynamic equilibrium even in the absence of a significant temperature gradient. The former, temperature cycling, experiments are more complex in that some of the solid silicon must dissolve in the liquid alloy during the heating part of the cycle and then recrystallize on the Si surface during the

cooling part of the cycle. These conditions simulate more closely the behavior of a silicon shell during cycling of encapsulated shot, although the stresses induced by volume expansion may be smaller than in spherical shot.

For analysis, the cooled samples will be sectioned, polished, and examined optically and by energy dispersive X-ray fluorescence in a scanning electron microscope (SEM-EDX). Electron excited X-ray dot maps of Al and of Si in a section will be used to determine the distribution of silicon and aluminum crystallites and the extent of interface degradation that has occurred.

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12.1.2 Solution Thermodynamics for Modeling Ideal Absorption Heat Pump Fluids

(J. Braunstein)

The aim of this work has been to develop representations of thermodynamic properties of mixtures to use in optimization programs for defining the characteristics of fluids which can provide the best possible coefficient of

performance (COP) in particular heat pump cycles.¹⁻³

Key properties are the temperature dependent and composition dependent vapor pressures, heats of vaporization, heat capacities, heats of mixing and activity coefficients.^{1,2} A stepwise approach has been taken towards a generalized treatment from simple but realistic representations.

The most reasonable one-parameter model for the activity coefficient is the regular solution (Hildebrand) model, with a temperature independent interaction parameter to represent the (symmetric) composition dependence of the excess free energy and excess enthalpy of the solution. Activity coefficients for known effective AHP fluids (which include very concentrated aqueous electrolytes such as LiBr-H₂O) generally have unsymmetric or skewed composition dependence.^{4,5} An additional parameter is thus needed in the composition dependence via, e.g., the Margules, van Laar, UNIQUAC or other representations.^{6,7} Temperature dependent excess enthalpy parameters are needed because they contribute to the difference between the heats of vaporization of refrigerant at the generator and at the absorber temperatures.

The smallest set of parameters that could account for most of the thermochemical properties of mixtures in a cycle is thus: vapor pressures and heats of vaporization of refrigerant and of absorbent (4 parameters); heat capacities of liquid and gaseous refrigerant and absorbent (4 parameters); activity coefficients and their composition and temperature dependence for solutions of refrigerant in absorbent (minimum of 3 parameters). Not included are fugacity coefficients of the mixed vapors, or the volumetric and kinetic properties which are related to heat and mass transfer. Means to be explored for possibly reducing the number of floated parameters include: (1) fix a particular absorbent (or a particular refrigerant) and optimize to find its best partner; (2) consider a non-volatile absorbent; (3) seek correlations among the

parameters that contribute most strongly to variations of heats of vaporization and heats of mixing.

Use of the optimized parameters to select improved refrigerant-absorbent pairs requires matching of the optimized parameters to data for real systems. Compilations of thermodynamic data are not noted for the uniqueness of their mathematical representation⁶ so that prudence in the matching of parameters will be required. It may be necessary to recast data representations for real systems into representations with fewer, more physically meaningful parameters, such as difference of heats of vaporization and of heats of mixing at upper and at lower temperatures of a cycle.

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12.1.3 Microemulsion Fuels

(A. L. Compere, W. L. Griffith, J. S. Johnson, Jr.¹, R. Triolo², E. Caponetti²)
Model Systems. In order to benefit from fundamental studies directed at determination of the structure of micelles and water-in-oil microemulsions, measurements on alcohol - hexadecane - water - ethanolamine - oleic acid

systems are being compared to similar measurements on the potassium oleate systems currently being studied by various collaborating groups (see Section 12.2). Components are systematically varied toward practical fuel compositions. Alcohol chain length, degree of neutralization, position of the fatty acid double bond, amount of water, and fraction of dispersed phase in these systems were varied. At concentrations of interest, scattering patterns are influenced by interparticle interactions. The structure functions for computing these effects, once the distribution departs from monodisperse spheres, are not well developed. Our observations clearly cannot be described by equations for monodisperse spheres. To reduce ambiguity in our inferences, we have developed equations allowing more accurate computation of the structure function for polydisperse distributions, the class for which present methods are least effective.³

Mathematical Analysis of Scattering Data from Polydisperse Systems. Previous investigators have used equivalent spheres to approximate the structure function for polydisperse systems. In order to avoid these approximations and to improve computing efficiency, an analytical expression for the static structure function of a polydisperse Percus-Yevick fluid with Schulz distributed particle diameters was developed. This result was extended to the full expression to obtain total scattering intensity.

Practical Fuel Systems. A factorial study designed to elucidate the effects of alcohol chain length, fatty acid mixture, water content, fatty acid neutralization, fuel type, and amount of dispersed phase content on microemulsion stability between 0 and 60°C was performed. The data indicate that the range of thermal stability increases with increasing alcohol chain length, decreasing water content, decreasing equivalent alkane carbon number of the fuel, increasing dispersed phase content, and increasing neutralization of fatty acids. The study, which used coconut, palm, and soy oil soapstocks in conventional fuel bases indi-

cated that microemulsion fuel systems stable across the temperature ranges typical of tropical areas could be produced.

Practical fuel composition development will generally be directed toward resolution of a specific combustion problem, such as emissions mitigation or use of an indigenous resource. To that end, a variety of different materials may be incorporated into base fuels ranging from gasoline to residual fuel oil and vegetable oil triglycerides. The required stability conditions for specific microemulsion fuels will be expected to reflect their target use.

The practical significance of microemulsion fuel systems is indicated by oil company interest in this area. ARCO Chemical Company is collaborating with us by providing combustion tests to measure emissions and performance of selected fuels. These will be performed using their extensive engine test facilities and skilled staff, with planned open literature publication of joint results.

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12.2 Small-Angle Neutron Scattering from Amphiphile Systems

(S. S. Berr,^{1,2} E. Caponetti,³ R. Triolo,³ L. J. Magid,⁴ R. M. Jones,^{1,5} J. B. Hayter,⁶ J. S. Johnson, Jr.⁷)

During the period of this report, emphasis in this cooperative program has been on comparisons of micelles of surfactants having straight and branched hydrocarbon chains, on micellar structure of aggregates formed of cationic vs. anionic surfactants, and on water-in-oil microemulsions. As examples, we shall present some

conclusions concerning hexadecyltrimethylammonium bromide (CTAB) aqueous solutions and potassium oleate-stabilized water-in-oil dispersions.

CTAB. In order to reduce ambiguity in the model inferred from scattering patterns, two sources of contrast (differences in scattering power) were employed: external, by varying the H_2O/D_2O ratio of the solvent; and measurements with both protiated and deuterated (D9) trimethyl ammonium head groups. The latter increased contrast between the core of the micelles, primarily comprised of the protiated hydrocarbon chain, and the shell separating the core from the continuous water region.

Figure 12.1 summarizes the patterns from 0.12 M CTAB-D9, plotted versus the momentum-transfer parameter, $Q = (4\pi/\lambda) \sin \theta$, λ being neutron wave-length ($4.75 \text{ \AA}$) and 2θ the scattering angle. The peaks in intensity indicate interparticle interference, expected

for ionic aggregated systems of this volume fraction. In the interpretation, the structure factors were computed by the mean spherical approximation.

The absence of fine structure in the high- Q region implied that the distribution was other than monodisperse spheres. We chose prolate ellipsoids as our model, to damp oscillations. The moderate axial ratios given by the least-squares fit (~ 1.5) leave open the alternative possibility of an oblate shape. Polydispersity would also smear out fine structure, but attempts to fit patterns with a Schulz distribution of spheres were not successful. The other aspects of the model were a dry hydrocarbon core, comprised only of the C_{16} hydrocarbon chains of the surfactant, and a shell comprised of headgroups, complexed bromides, and water, computed from literature hydration numbers of tetramethyl ammonium and bromide ions. An alternative model, in which

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CTAB-D9 EXTERNAL CONTRAST VARIATION

Fig. 12.1. Small-angle neutron scattering from 0.12 M cetyl trimethylammonium(D9) bromide solutions as a function of isotopic composition of water. Curves computed for prolate ellipsoids, with MSA structure function.

the semi-minor axis was fixed at the extended length of the C_{16} chain, the shell thickness allowed to vary, and the remaining volume of the shell filled with water, gave equivalent fits and essentially the same results.

The micellar parameters varied were the number of surfactant molecules/micelle, the micellar charge, and the axial ratio. From these and known volumes of the groups were computed the radius of the core (corresponding to a sphere of equivalent volume) and the radius of the equivalent total particle. The computed curves in the figure are in good agreement, and equivalently good fits with similar parameters were obtained for perprotiated surfactant over the external contrast range covered, from 100% to 35% H_2O .

Our conclusions agree with those from SANS studies on C_{12} and C_{14} trimethyl ammonium bromide micelles,⁸⁻¹⁰ in that the micelle core appears to be dry. In this respect, our measurements indicate that anionic micelles are different; there seems to be considerable interpenetration of water and hydrocarbon in the outer part of sodium dodecyl sulfate and sodium dodecylphenylsulfonate (especially with branched chains) micelles. Our degrees of aggregation (~ 145 monomers/micelle) follow the trend reported for shorter-chain-length trimethyl ammonium bromides: 110 for C_{14} and 68 for C_{12} . Charges were in the neighborhood of 25/micelle.

There is a significant drift downward in aggregation number with increasing H_2O ratio, for both the D9 and perprotiated surfactants; with the D9, the value dropped from 146 for D_2O to 127 for H_2O (the corresponding equivalent core radii changed from 25.2 to 24 Å). At this chain length, there appears to be an effect of the isotopic composition of the solvent on aggregate size; the critical micelle concentration is also lower in heavy water.

Water-in-oil microemulsions. These are interesting chemical systems, important in development of enhanced-oil-recovery technology, of microemulsion fuels (see 12.1.3), and of catalytic processes, among other prac-

tical areas. The system of interest here has received considerable attention by other techniques;¹¹⁻¹⁷ it is comprised of hexadecane/potassium oleate/water/1-pentanol or 1-hexanol. The approximate mole ratios of other components to potassium oleate were 5.5 for hexadecane, 6 for pentanol, and 5 for hexanol. Water in the pentanol case was varied from 18 to 57, or volume fractions of 11 to 29%; the single hexanol composition contained 45 moles D_2O per oleate.

The scattering patterns (Figures 12.2 and 12.3) all have peaks in intensity vs. angle, an indication of excluded-volume (because water-in-oil micelles are uncharged) interparticle structure effects. These patterns establish without recourse to model that organized structures exist at all of these compositions, of dimensions characterized by distances of the order of a few tens of angstroms. Although there is considerable disagreement in the literature cited, many of the authors concluded that over at least some of the composition ranges we covered, the surfactant, water, and alcohol were molecularly dispersed in hexadecane.

It seems highly probable a priori that, if closed aggregates are present, they will be comprised of an aqueous core, surrounded by a layer of surfactant and alcohol. In evolving a model giving satisfactory fits, we found it necessary to allow in computation of the structure function for penetration of the outer surfactant layer of the aggregates by hydrocarbon from the continuous phase or from other aggregates. With respect to particle geometry, we obtained with oblate ellipsoids much better fits than with prolate ellipsoids or with monodisperse or polydisperse spheres. The fits shown are for this shape. Figure 12.2 is for three solutions of approximately the same composition, except that in I the contrast is provided by D_2O , in II by $C_{16}D_{34}$, and in III, by both heavy water and deuterated hexadecane, the shell being highlighted. Good fits with parameters of comparable magnitude were obtained with I and II, but only the general

The fits to other compositions (Fig. 12.3) by the model were good. There are no obvious variations in structure correlating with some surprising differences in electrical properties reported for various compositions in some of the cited references. The core radii increased from 18 Å for 18 waters/potassium oleate to 37 Å for a ratio of 57, when pentanol was the cosurfactant. In presence of hexanol and 45 waters per surfactant, the core radius was 38 Å, compared to 33 for a similar composition with pentanol.

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12.3 Raman Spectroscopic Studies of UO_2^{2+} Association with Hydrolytic Species of Group IV Metals

(S. A. Sherrow,¹ G. M. Begun)

Hydrolysis dominates the aqueous chemistry of the quadrivalent metals. Complexation, ion exchange, and solubility properties of the metals are profoundly affected by the presence of mono- and polynuclear hydrolysis products. The distribution of hydrolytic species is a complicated function of metal concentration, solution acidity, and concentration and identity of additional ions. In many cases, the chemistry is further complicated by the slow

Fig. 12.3. Small-angle neutron scattering from water-in-oil microemulsions of different compositions. D₂O-surfactant mole ratios, cosurfactant 1-pentanol: A, 18; B, 45; C, 57. 1-hexanol: C, 45.

aggregation of hydrolysis products into polymeric hydroxides, which eventually precipitate from solution. An example of a particularly troublesome condition is the polymerization and precipitation of Pu(IV) in nuclear fuel reprocessing streams. Most published studies of hydrolysis treat the behavior of a single metal ion in noncomplexing media. Solutions in commercial processes are less ideal and often contain appreciable concentrations of several metal ions. In such systems, interactions between hydrolytic species may significantly alter the chemical behavior of the species of interest. Raman spectra are especially useful in examining the actual species present in aqueous solutions.

Previously² we have studied, by means of Raman spectral observations, the hydrolytic behavior of uranyl (UO_2^{2+}) ions as the pH of an aqueous solution was varied. Toth et al.³ at ORNL have also shown that Pu(IV) polymerization and precipitation are inhibited by the presence of uranyl ion. Our Raman spectroscopic studies⁴ revealed that addition of uranyl ions to hydrolyzing Th(IV) solutions results in the formation of a hydroxyl-bridged UO_2^{2+} -Th(IV) complex which, upon mild heating, is converted to a uranate-like species. The present study is an extension of that work to the hydrolysis of Zr(IV)/ UO_2^{2+} solutions. Solutions of Hf(IV) were also examined, as were uranyl-loaded, solid hydrous oxides. We use the term "solution" somewhat loosely as the extensively hydrolyzed samples are more properly referred to as well-dispersed sols.

The Raman spectra were recorded at the Chemistry Division's Raman facility in Bldg. 5505. Excitation of the spectra was accomplished with the 514.5 nm line of an argon-ion laser or with the 647.1 nm line of a krypton-ion laser. Baseline subtraction and peak integration were performed on an IBM 9000 computer. The intensity of the water bending vibration at 1640 cm^{-1} was used for approximate normalization of the data.

Raman spectra ($300\text{--}700\text{ cm}^{-1}$) of Zr(IV) at various stages of hydrolysis are shown in

Fig. 12.4. Spectra of crystalline $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and amorphous hydrous zirconia are included for comparison. The Raman spectra of oriented single crystals of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ revealed that as many as six bands, predominantly Zr-O(H)

Fig. 12.4. Raman spectra of (a) crystalline $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$; (b) 0.50 M Zr(IV) in 1 M HCl; (c) 0.50 M Zr(IV), pH ~0.4; (d) 0.50 M Zr(IV), pH ~0.7; and (e) amorphous hydrous zirconia, " Zr(OH)_4 ". The higher frequency band is polarized. Excitation 514.5 nm.

stretches, contribute to the spectrum shown in Fig. 12.4a. The progressive shift to lower wavenumber is due to simultaneous replacement of coordinated water molecules by hydroxyl and aggregation of the tetramers into polymeric sheets.

Acidic solutions containing Zr(IV) and uranyl ions yielded spectra closely resembling those of the separate components. As solution pH was increased, however, a new polarized Raman band appeared at 835 cm^{-1} in these mixtures. Representative spectra are shown in Fig. 12.5. The increased intensity at 835 cm^{-1} was accompanied by a decrease in intensity of the 872 cm^{-1} band assigned to "free" hydrated uranyl ion, or "monomer". In addition, at constant uranyl ion concentration, the intensity of the 835 cm^{-1} band increased as the Zr(IV) ion concentration was increased. Assignment of the band at 835 cm^{-1} to a pure uranyl hydrolysis product was ruled out by its frequency and by the acidity of the solution. The 853 cm^{-1} band characteristic of uranyl "dimer", $(\text{UO}_2)_2(\text{OH})_2^{2+}$, was observed only in the spectrum of the most basic solution (Fig. 12.5d). We therefore assigned the 835 cm^{-1} band to ν_1 of UO_2^{2+} complexed by the Zr(IV) hydrolytic species. A similar 835 cm^{-1} band was also observed in the spectra of hydrolyzed Hf(IV)/ UO_2^{2+} solutions. In the hydrolyzed Th(IV) solutions described previously,⁴ ν_1 of complexed uranyl ion was observed at 851 cm^{-1} . The low wavenumber spectra of solutions containing the complexed uranyl ion were similar to Fig. 12.4d, although shifted slightly to lower wavenumber due to the greater Zr(IV) aggregation in these solutions. No bands attributable to the U-O(H) stretching vibration were observed, but such bands are generally very weak.

A substantial decrease in pH (0.8-1.5 pH units) was recorded for heated solutions or solutions maintained for several months at room temperature. Solutions prepared with pH > 3 yielded a precipitate when heated. The 835 cm^{-1} band was greatly diminished or altogether absent from the spectra of heated solutions and

Fig. 12.5. Effects on the Raman spectra of increasing pH in a solution of 0.25 M Zr(IV) and 0.10 M UO_2^{2+} : (a) pH = 1.71, (b) pH = 2.06, (c) pH = 2.53, and (d) pH = 2.98. Both bands are polarized. Excitation 514.5 nm.

the intensity of the 872 cm^{-1} band was increased accordingly.

These results are different from those of the Th(IV) studies.⁴ Although hydrolyzed Th(IV)/ UO_2^{2+} solutions exhibited a similar pH decrease when heated, they underwent a dramatic

color change from yellow to orange. The intensity of the band assigned to complexed uranyl ion was greatly diminished in the Raman spectra of these solutions, while the band assigned to free uranyl ion showed only a slight increase. A new, broad, polarized band was observed at 665 cm^{-1} which we ascribed to the symmetric U-O stretch of a uranate-like species.

Complexation of uranyl ion by polynuclear hydrolytic species is clearly related to adsorption by solid hydrous oxides. The cation exchange properties of the hydrous oxides are due to the acidic character of the metal hydroxyl groups. In these solids double oxygen bridges bind uranium atoms to metal atoms at the hydrous oxide surface. Hydrous oxides and uranyl-loaded hydrous oxides of Zr(IV), Hf(IV), and Th(IV) were prepared. Their Raman spectra are shown in Fig. 12.6. Other than ν_1 (observed at $820\text{--}822\text{ cm}^{-1}$) no bands attributable to uranyl were observed in the spectra of the solids. The frequencies we observed for the ν_1 vibration of UO_2^{2+} complexed in solution by the M(IV) ion are 835 , 835 , and 851 cm^{-1} for Zr(IV), Hf(IV) and Th(IV), respectively. At the compositions of the solutions employed in the sorption experiments, it is unlikely that the adsorbed uranyl species were polynuclear or contained additional hydroxyl ligands. The observed ν_1 frequencies are appropriate for uranyl coordinated by two bridging oxygens, and the differences in the observed frequencies are insignificant. The spectra shown in Fig. 12.6 clearly indicate that the adsorbed uranyl species is bound similarly to hydrous ZrO_2 , HfO_2 , and ThO_2 . The Zr(IV)/ UO_2^{2+} and Hf(IV)/ UO_2^{2+} solution spectra, however, are distinctly different from the Th(IV)/ UO_2^{2+} spectra, and the behavior of the heated Th(IV)/ UO_2^{2+} solutions is drastically different.

Essentially all Zr(IV) in solution is present as the cyclic tetramer at acid concentrations of 1 molar or above.⁵ In the pH region where uranyl attachment is observed, the tetramers are extensively aggregated (i.e., polymeric). The polymer structure is closely related, if not identical, to that of the solid hydrous

Fig. 12.6. Raman spectra of hydrous oxides and UO_2^{2+} loaded hydrous oxides: (a) loaded ZrO_2 , (b) ZrO_2 , (c) loaded HfO_2 , (d) HfO_2 , (e) loaded ThO_2 , and (f) ThO_2 . Excitation 647.1 nm .

oxide. The 835 cm^{-1} frequency observed for UO_2^{2+} in the hydrolyzed solutions is 15 cm^{-1} lower than that observed in doubly hydroxyl-bridged uranyl dimer. We thus conclude that the complexation of uranyl by the hydrolyzed Zr(IV) is essentially due to adsorption, and that the uranium atom is bound by double oxygen bridges or by extremely acidic double hydroxyl bridges. The 12 cm^{-1} decrease in ν_1 observed for the hydrous oxide is not unreasonable for the transition from solution to solid state.

Heating the hydrolyzed Zr(IV) solutions promotes condensation and crystallization of the Zr(IV) species, reducing the number of sites available to uranyl and decreasing the pH of the solution. The result is desorption of uranyl and exclusion from the stable structure. The substantial differences in the behavior of the Th(IV)/UO₂²⁺ and Zr(IV)/UO₂²⁺ systems are explicable, but could not have been predicted from the available data on hydrolysis of the individual species.

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SEPARATIONS CHEMISTRY

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CATALYSIS

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NUCLEAR WASTE CHEMISTRY

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- A. L. Compere, W. L. Griffith, and J. M. Googin,¹ "Integrated Palm Oil Processing," pp. 515-522 in Alternative Energy Sources VI, Vol. 2, ed. T. N. Veziroglu, Washington, DC, Hemisphere Press, Inc., 1984.
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DIVISIONAL STAFFING AND FINANCIAL SUMMARY
FY 1985

Funding source	Financial plan (\$K)	Direct scientific and technical staff (full-time equivalents)
DOE PROGRAMS		
Basic Energy Sciences		
Nuclear Sciences	\$1,238	6.1
Materials Sciences	2,207	15.0
Chemical Sciences	3,286	23.4
Geosciences	466	3.0
Conservation	<u>133</u>	<u>1.0</u>
TOTAL DOE PROGRAMS	\$7,330	48.5
WORK FOR OTHERS PROGRAMS		
Nuclear Regulatory Commission	\$ 430	3.5
Department of Treasury	181	1.0
Department of Defense	26	0.2
Other Oak Ridge Plants	<u>100</u>	<u>0.9</u>
TOTAL WORK FOR OTHERS	\$ 737	5.6
TOTAL FINANCIAL PLAN	\$8,067	54.1

Divisional staff	Number (full-time equivalents)
Scientific and technical	
Direct	54.1
Indirect	6.8
On loan to other Divisions	7.4
Support	<u>8.5</u>
TOTAL	76.8

CHEMISTRY DIVISION

February 1, 1986

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